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Seasonal, Latitudinal, and Secular Variations in the Abundance and Isotopic Ratios of Atmospheric Carbon Dioxide

1. Results From Land Stations

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Between March 1977 and February 1982, 517 samples of air were collected in 5 l glass flasks at four stations in the northern hemisphere near the Pacific ocean and at the South Pole. First, the CO_2 concentration of each sample was determined by nondispersive infrared gas analysis, and then the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the cryogenic extracted CO_2 were determined with a triple collector mass spectrometer. For each station the secular trend and seasonal variation in $^{13}\text{C}/^{12}\text{C}$ ratio have been established as a function of CO_2 concentration. The seasonally adjusted $^{13}\text{C}/^{12}\text{C}$ ratio is found to have decreased at a rate of about 0.02‰ per ppm increase in the seasonally adjusted CO_2 concentration and to vary with latitude as expected if CO_2 is being released by fossil fuel combustion in the northern hemisphere and from ocean water near the equator. At the three northernmost stations (La Jolla, California, at 33°N and two Hawaiian stations near 19°N) the $^{13}\text{C}/^{12}\text{C}$ ratio of the CO_2 added to and withdrawn from the atmosphere during one annual cycle is circa –29‰ with respect to standard PDB, as expected from the exchange of atmospheric CO_2 with the carbon of terrestrial plants. Near the equator at Fanning Island (4°N) the similarly computed $^{13}\text{C}/^{12}\text{C}$ ratio is –21‰, while at the South Pole it is about –13‰. This suggests that the seasonal variation in the southern hemisphere and tropics is partially a result of oceanic CO_2 exchange.

INTRODUCTION

The carbon of fossil fuels is depleted in ^{13}C with respect to atmospheric CO_2 [Tans, 1981]. Therefore, an increase in concentration of atmospheric CO_2 brought about by fuel combustion will be accompanied by a year to year decrease in $^{13}\text{C}/^{12}\text{C}$ ratio of the CO_2 . Isotopic exchange with the oceans reduces the rate of this isotopic shift with concentration to about one third of what would occur if all fossil fuel CO_2 remained airborne [Keeling *et al.*, 1980]. A precise knowledge of the actual shift may add to our understanding of the global carbon cycle, because the activity of the land biosphere also affects atmospheric CO_2 , but with a different isotopic shift for a given change in atmospheric CO_2 concentration. The possible isotopic shifts are slight, however, and only very precise measurements over a decade or more will permit a discrimination to be made between long-term oceanic and biospheric effects [Keeling *et al.*, 1980]. The present study extends our previous measurements [Keeling *et al.*, 1979] to 4 years in both hemispheres and thus long enough to indicate the feasibility of obtaining precise long-term records but still too short to provide definitive answers.

Detection of the year to year shift in the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 is complicated by seasonal variations which accompany the uptake and release of CO_2 by terrestrial vegetation and soils during photosynthesis and respiration. Since the amplitude and phase of the seasonal variation in CO_2 concentration have been found to be nearly constant in time wherever we have made isotopic measurements, we postulate that the $^{13}\text{C}/^{12}\text{C}$ ratios at these locations also vary seasonally

to nearly the same extent each year. At each station discussed here the record is long enough to establish the average isotopic seasonal cycle quite precisely. Assuming that this typical cycle was repeated during each year of record at each station, we have used an iterative procedure to separate the seasonal component of the observed trend in $^{13}\text{C}/^{12}\text{C}$ ratio from the long-term trend attributed to fossil fuel combustion.

We report here the results of sampling air at La Jolla, California (32.9°N, 117.3°W); Mauna Loa Observatory, Hawaii (19.5°N, 155.6°W); Cape Kumukahi, Hawaii (19.5°N, 154.8°W); Fanning Island (3.9°N, 159.3°W); and at the South Pole. Additional data were obtained from samples collected on ships between 20°N and 17°S on the First Global Geophysical Experiment (FGGE), during A.D. 1979 and 1980. These will be reported in a separate paper. [Keeling *et al.*, 1983]. Also, descriptions of the sites will be separately reported in articles dealing with the full records of CO_2 concentration at each station.

EXPERIMENTAL DETAILS

Typically, two or three samples of air are collected at each location twice per month. The air is sucked into previously evacuated 5 l flasks closed off with high vacuum Apiezon greased stopcocks. After collection, the samples are returned to the Scripps Institution of Oceanography where each flask is analyzed twice for the CO_2 concentration using an infrared analyzer according to procedures described by Keeling *et al.* [1968]. Samples collected at La Jolla, however, are only analyzed once because a large number of samples assures a negligible mean error from analysis. The CO_2 remaining in each flask after infrared analysis is extracted by pumping the residual air through a large spherical liquid nitrogen trap at a pressure of 1–10 mm of mercury. The condensate is freed from

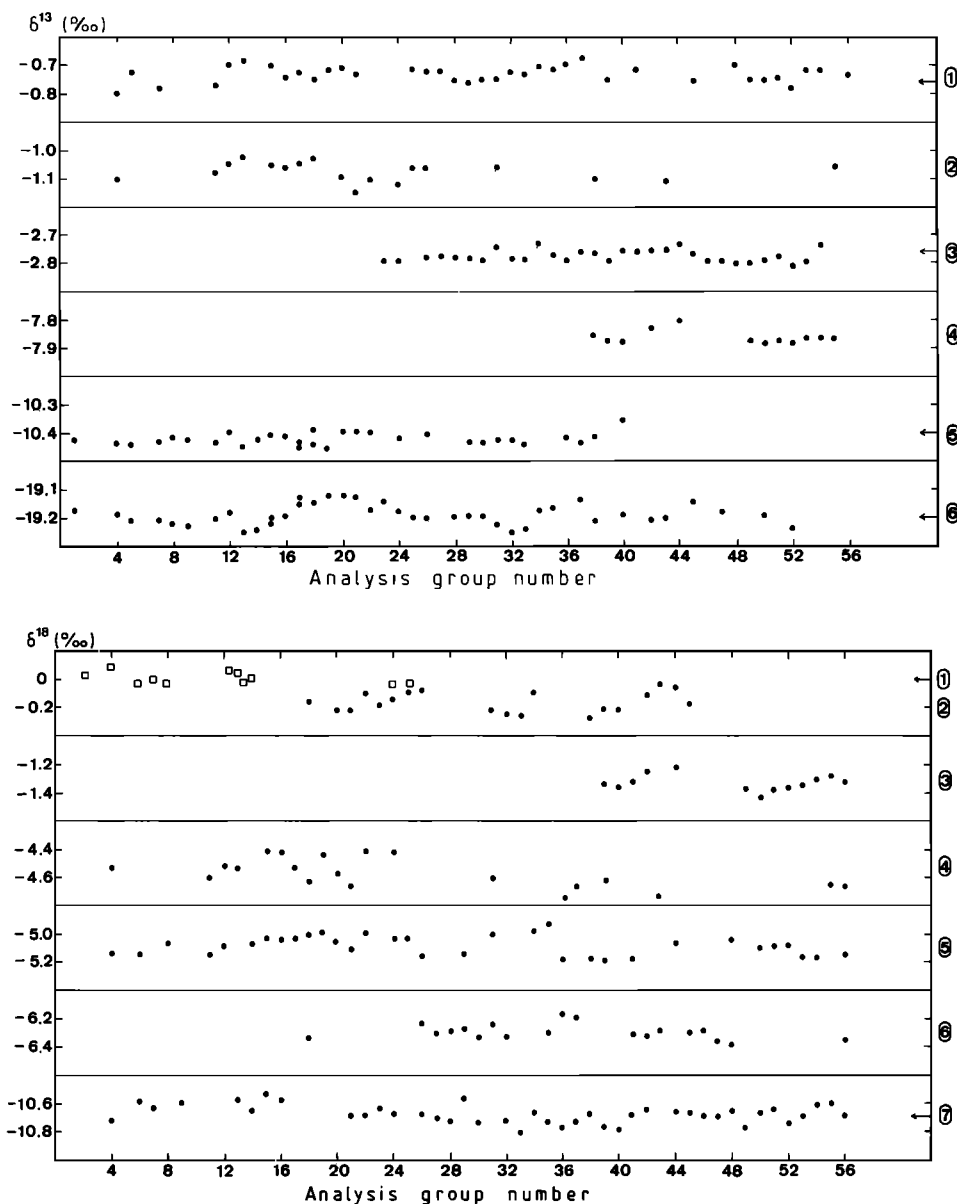


Fig. 1. δ^{13} and δ^{18} of isotopic standards in use during the project. Typically, several standards were analyzed together with the samples of one shipment, here designated by analysis group number. Arrows indicate mean values of standards analyzed over a period of at least 10 years. (a) The mean values for standards 1, 2, 3, and 6 are derived from analyses from A.D. 1963–1969 inclusive. Standard 4 was established during the present study; the mean value (not shown) is for A.D. 1981–1982. Standard 5 was established during the ^{14}C intercomparison in A.D. 1972; the mean value is -10.40 ‰. Standards 1, 3, and 4 are laboratory materials and 2 and 6 are NBS 20 and oxalic acid I, respectively, obtained from the U.S. National Bureau of Standards; standard 5 is ANU sucrose obtained from H. Polach. (b) Standard 1 (plotted as squares) is V-SMOW, of which δ^{18} is equal to 0 ‰ by definition. Standards 2 and 6 are laboratory water standards, of which δ^{18} is given relative to V-SMOW. δ^{18} values of other standards are given relative to PDB-CO₂. Standards 3, 4, 5, and 7 are the same as those mentioned under Figure 1a as 4, 2, 1, and 3, respectively. Although NBS20 (nr. 4) is a primary standard, the δ^{18} value has changed significantly during the last 15 years and has no longer the original value of -4.14 ‰.

water vapor by fractional sublimation at dry ice temperature, and the resulting gas is transferred to a sample tube for shipment to the Isotopic Physics Laboratory in Groningen. The apparatus and procedures for extraction of CO₂ follow closely those used by Keeling [1958, 1961] in an earlier study of the isotopic composition of atmospheric CO₂. In the case of the samples collected at the South Pole, the contents of two flasks are extracted together because too little gas remains in a single flask for mass spectrometric analysis. Otherwise, individual flask samples are extracted.

Two types of stopcocks have been used as closures for the

small isotopic sample tubes used to ship samples to Groningen. At the beginning of the study, pyrex glass vials closed off with a 4-mm bore ground glass stopcock were used. These were lubricated in the normal fashion with Apiezon-N high vacuum grease. Later on, these were replaced with vials having high vacuum O-ring stopcocks with a 9-mm orifice (manufactured by Louwers Hapert B.V., The Netherlands). The O-rings are very slightly greased with Apiezon-N. The vacuum properties of the newer vials are comparable to those having glass stopcocks, with the additional advantages of a low pumping resistance and ease in opening and closing. Ac-

TABLE 1. Air Samples Collected at La Jolla

| Date | Isotopic Analysis Group Number | Number of Analysis | Average CO ₂ Concentration, ppm | Standard Deviation, ppm | CO ₂ Trend, ppm | Average Carbon 13/12, ‰ | Standard Deviation, ‰ | Average Oxygen 18/16, ‰ | Standard Deviation, ‰ |
|----------------|--------------------------------|--------------------|--|-------------------------|----------------------------|-------------------------|-----------------------|-------------------------|-----------------------|
| April 1, 1978 | 1 | 11 | 339.11 | 0.17 | 335.52 | -7.93 | 0.02 | -0.04 | 0.19 |
| June 27, 1978 | 2, 3 | 11 | 334.94 | 0.17 | 335.78 | -7.71 | 0.04 | +0.15 | 0.10 |
| June 27, 1978 | 3 | 1 | 335.00* | — | — | -8.09* | — | -0.64* | — |
| Aug. 22, 1978 | 4 | 4 | 331.37 | 0.13 | 336.08 | -7.45 | 0.05 | -0.24 | 0.18 |
| Sept. 7, 1978 | 4 | 9 | 329.39 | 0.06 | 336.25 | -7.34 | 0.06 | -1.01 | 0.14 |
| Sept. 7, 1978 | 4 | 1 | 329.52* | — | — | -7.15* | — | -0.39* | — |
| Sept. 7, 1978 | 4 | 1 | 329.43* | — | — | -7.11* | — | -0.73* | — |
| Sept. 7, 1978 | 4 | 1 | 329.34* | — | — | -7.92* | — | -2.29* | — |
| Nov. 1, 1978 | 5 | 11 | 335.50 | 0.13 | 336.63 | -7.71 | 0.04 | -0.57 | 0.19 |
| Jan. 17, 1979 | 6 | 12 | 340.81 | 0.14 | 337.02 | -7.98 | 0.06 | -0.20 | 0.17 |
| Jan. 25, 1979 | 6 | 3 | 338.65 | 0.10 | 337.02 | -7.90 | 0.02 | -0.46 | 0.11 |
| Jan. 25, 1979 | 6 | 1 | — | — | — | -7.89† | — | -0.23† | — |
| Jan. 25, 1979 | 6 | 1 | — | — | — | -7.88† | — | -0.21† | — |
| Feb. 23, 1979 | 7, 9 | 10 | 339.12 | 0.09 | 337.20 | -8.05 | 0.06 | -0.79 | 0.16 |
| Feb. 23, 1979 | 7 | 1 | 339.05* | — | — | -8.37* | — | -2.05* | — |
| April 17, 1979 | 8, 9 | 10 | 341.18 | 0.08 | 337.56 | -8.15 | 0.04 | -1.02 | 0.21 |
| Aug. 29, 1979 | 13, 14 | 10 | 332.95 | 0.04 | 338.38 | -7.59 | 0.05 | -0.81 | 0.08 |
| Nov. 19, 1979 | 16 | 10 | 339.45 | 0.10 | 338.84 | -8.04 | 0.04 | -1.11 | 0.06 |
| Nov. 19, 1979 | 16 | 1 | 339.43* | — | — | -8.23* | — | -1.11* | — |
| March 12, 1980 | 21, 22 | 6 | 340.84 | 0.10 | 339.11 | -7.99 | 0.09 | -0.70 | 0.16 |
| Aug. 12, 1980 | 25 | 12 | 333.94 | 0.18 | 339.61 | -7.58 | 0.09 | -1.04 | 0.12 |
| Oct. 15, 1980 | 31 | 6 | 337.61 | 0.04 | 339.95 | -7.76 | 0.02 | -1.44 | 0.12 |
| Dec. 5, 1980 | 31, 32 | 6 | 340.45 | 0.04 | 340.33 | -7.89 | 0.02 | -1.38 | 0.07 |
| Jan. 30, 1981 | 32 | 11 | 342.42 | 0.05 | 340.53 | -8.05 | 0.06 | -1.36 | 0.23 |
| Feb. 26, 1981 | 32, 34 | 11 | 343.87 | 0.05 | 340.71 | -8.09 | 0.02 | -1.20 | 0.09 |
| May 20, 1981 | 34, 36 | 12 | 344.47 | 0.07 | 341.08 | -8.11 | 0.03 | -0.89 | 0.14 |
| July 1, 1981 | 38 | 6 | 339.94 | 0.06 | 341.24 | -7.82 | 0.03 | -0.76 | 0.11 |
| Aug. 31, 1981 | 40 | 12 | 336.21 | 0.08 | 341.30 | -7.64 | 0.02 | -0.89 | 0.12 |
| Sept. 24, 1981 | 42 | 4 | 337.79 | 0.04 | 341.36 | -7.61 | 0.08 | -1.12 | 0.11 |
| Oct. 5, 1981 | 42 | 6 | 338.10 | 0.13 | 341.42 | -7.67 | 0.06 | -1.16 | 0.08 |
| Nov. 6, 1981 | 47 | 6 | 339.54 | 0.00 | 341.50 | -7.82 | 0.02 | -1.05 | 0.03 |
| Dec. 21, 1981 | 56 | 5 | 342.24 | 0.02 | 341.62 | -7.98 | 0.03 | -1.10 | 0.10 |
| Average | | | | 0.09 | | | 0.04 | | 0.12 |

*Individual analyses rejected from data averaged for that day.

†Special storage test: no concentration analyses performed.

cording to our experience in handling ¹⁴C samples in Groningen, the chances of contamination and memory effect are smaller with O-ring stopcocks owing to the much smaller amount of grease.

Tests with pure CO₂ indicated no changes in ¹³C/¹²C ratio in samples stored in the O-ring sample tubes for 1 year. This result is consistent with our earlier experience with glass stopcock sample tubes, which also showed no isotopic changes on storage. The CO₂ gas, stored in sample tubes, was shipped in groups of 20–40 tubes to the Groningen Laboratory. The shipments were numbered consecutively. The storage time between extraction and isotopic analysis usually was between 1 and 3 months, but occasionally was as short as 20 days or as long as 6½ months.

The mass spectrometric analyses were carried out in the Groningen laboratory by using a VG micromass 903 spectrometer. Corrections for the abundance of ¹⁷O have been applied by using procedures described by Mook and Grootes [1973]. Usually all samples in a given shipment were analyzed in a batch. We designate these groups of analyses by "isotopic analysis group numbers" corresponding to the shipment numbers.

In many cases the samples were also analyzed for N₂O on separate aliquots withdrawn from the flasks before extraction of the CO₂. These analyses, carried out by gas chroma-

tography, using a methanizer and flame ionization detection, are reported by Weiss [1981].

CORRECTION FOR N₂O

As discussed by Craig and Keeling [1963], if liquid N₂ is used to extract atmospheric CO₂ cryogenically, the presence of N₂O in an air sample interferes with the mass spectrometric analysis of the extracted CO₂, since the N₂O is not separated from the CO₂ and has the same isotopic masses (44, 45, 46) as CO₂. For a mole fraction of nitrous oxide of 300 ppb of dry air, which is typical at remote stations [Weiss, 1981], one obtains a correction of about +0.32‰. We applied this number in our previous publication to obtain the ¹³C/¹²C ratio of atmospheric CO₂ [Keeling et al., 1979]. More recently, Mook and Van der Hoek [1983] have shown that the mass spectrometer used at Groningen is less sensitive for N₂O than for CO₂. At equal inlet pressures the mass 44 ion beam intensity of N₂O⁺ is about 73% of that of CO₂⁺. Consequently, the expected N₂O correction is only about +0.225‰.

To verify this prediction, we determined the shift in ¹³C/¹²C ratio when the N₂O is removed quantitatively from our samples by circulation over hot copper pellets at 700°C. The observed average correction based on results from 247 samples is +0.18 ± 0.06‰.

TABLE 2. Air Samples Collected at the Mauna Loa Observatory

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| June 30, 1978 | 2 | 4 | 337.09* | 335.12* | -7.62* | 0.65* |
| July 14, 1978 | 2 | 4 | 336.49* | 335.22* | -7.58* | 0.58* |
| July 28, 1978 | 2 | 4 | 335.72* | 335.22* | -7.47* | 0.67* |
| Aug. 11, 1978 | 2 | 4 | 334.34* | 335.33* | -7.41* | 0.71* |
| Sept. 1, 1978 | 2 | 4 | 333.14* | 335.43* | -7.11* | 0.83* |
| Sept. 15, 1978 | 2 | 4 | 332.10* | 335.43* | -7.41* | 0.19* |
| Nov. 16, 1979 | 2 | 18 | 335.87* | 337.25* | -7.98* | -2.11* |
| Nov. 30, 1979 | 2 | 18 | 335.87* | 337.25* | -7.89* | -1.61* |
| Dec. 14, 1979 | 2 | 18 | 337.01* | 337.42* | -8.10* | -1.83* |
| Feb. 15, 1980 | 2 | 20 | 339.21 | 337.76 | -7.98 | -1.69 |
| Feb. 29, 1980 | 2 | 20 | 339.48 | 337.76 | -7.86 | -1.94 |
| March 14, 1980 | 2 | 20 | 340.05 | 337.91 | -8.01 | -2.03 |
| March 28, 1980 | 2 | 21 | 340.77 | 337.91 | -7.90 | -1.44 |
| April 18, 1980 | 2 | 21 | 340.31 | 338.06 | -7.88 | -1.21 |
| May 2, 1980 | 2 | 21 | 341.72 | 338.19 | -7.91 | -1.05 |
| May 16, 1980 | 2 | 22 | 341.43 | 338.19 | -7.93 | -1.44 |
| May 30, 1980 | 2 | 22 | 341.13 | 338.19 | -7.96 | -1.09 |
| June 27, 1980 | 2 | 26 | 340.20 | 338.32 | -7.98 | -0.38 |
| July 18, 1980 | 2 | 26 | 338.22 | 338.44 | -7.69 | -0.30 |
| Aug. 1, 1980 | 2 | 26 | 338.14 | 338.56 | -7.65 | -0.34 |
| Aug. 11, 1980 | 2 | 26 | 338.10 | 338.56 | -7.59 | -0.06 |
| Sept. 5, 1980 | 2 | 26 | 337.41 | 338.67 | -7.70 | -0.06 |
| Sept. 19, 1980 | 2 | 26 | 335.54 | 338.67 | -7.56 | -0.43 |
| Oct. 3, 1980 | 2 | 26 | 335.71 | 338.77 | -7.51 | -0.25 |
| Oct. 17, 1980 | 2 | 28 | 336.33 | 338.77 | -7.71 | -1.05 |
| Oct. 31, 1980 | 2 | 28 | 337.14 | 338.77 | -7.70 | -0.81 |
| Nov. 14, 1980 | 2 | 28 | 337.31 | 338.87 | -7.64 | -0.27 |
| Nov. 28, 1980 | 2 | 28 | 337.87 | 338.87 | -7.64 | -0.82 |
| Dec. 19, 1980 | 2 | 28 | 339.23 | 338.97 | -7.75 | -0.69 |
| Jan. 9, 1981 | 2 | 28 | 339.39 | 339.06 | -7.72 | -0.70 |
| Jan. 23, 1981 | 2 | 36 | 339.93 | 339.06 | -7.79 | -1.09 |
| Feb. 6, 1981 | 2 | 36 | 341.42 | 339.15 | -7.82 | -1.55 |
| Feb. 20, 1981 | 2 | 36 | 339.47 | 339.15 | -7.70 | -0.95 |
| April 17, 1981 | 2 | 38 | 343.61 | 339.30 | -7.94 | -0.74 |
| May 15, 1981 | 2 | 38 | 343.16 | 339.36 | -8.03 | -0.91 |
| May 29, 1981 | 2 | 40 | 342.75 | 339.36 | -8.00 | -0.42 |
| June 12, 1981 | 2 | 40 | 342.73 | 339.41 | -7.97 | -0.66 |
| June 26, 1981 | 2 | 40 | 341.57 | 339.41 | -7.92 | -0.33 |
| July 17, 1981 | 2 | 42 | 338.20* | 339.46* | -7.50* | -0.06* |
| Aug. 14, 1981 | 2 | 42 | 338.83 | 339.51 | -7.71 | -0.39 |
| Aug. 21, 1981 | 2 | 42 | 336.16* | 339.51* | -7.30* | -0.52* |
| Aug. 28, 1981 | 2 | 47 | 337.66 | 339.51 | -7.59 | -0.58 |
| Sept. 4, 1981 | 2 | 47 | 337.04 | 339.57 | -7.54 | -0.66 |
| Sept. 11, 1981 | 2 | 47 | 337.15 | 339.57 | -7.63 | -0.76 |
| Sept. 18, 1981 | 2 | 47 | 337.11 | 339.57 | -7.59 | -0.52 |
| Sept. 25, 1981 | 2 | 47 | 336.67 | 339.57 | -7.58 | -0.65 |
| Oct. 2, 1981 | 2 | 47 | 336.57* | 339.62* | -7.98* | -1.46* |
| Oct. 30, 1981 | 2 | 51 | 337.47 | 339.62 | -7.57 | -0.63 |
| Nov. 6, 1981 | 2 | 51 | 337.79 | 339.69 | -7.63 | -0.73 |
| Dec. 4, 1981 | 2 | 56 | 339.40 | 339.76 | -7.72 | -0.67 |
| Dec. 18, 1981 | 2 | 56 | 339.74 | 339.76 | -7.74 | -0.60 |
| Dec. 28, 1981 | 2 | 56 | 340.44 | 339.76 | -7.78 | -0.92 |
| Jan. 8, 1982 | 2 | 56 | 339.76 | 339.82 | -7.70 | -0.44 |
| Jan. 29, 1982 | 2 | 56 | 341.18 | 339.82 | -7.81 | -0.52 |
| Feb. 5, 1982 | 2 | 56 | 341.45 | 339.88 | -7.85 | -0.58 |
| Feb. 12, 1982 | 2 | 56 | 341.22 | 339.88 | -7.79 | -0.24 |

*Rejected.

Because the ratio between the N₂O and CO₂ concentration is nearly constant in our samples, we propose a correction of +0.225‰ for all ¹³C/¹²C ratios in the present study. A corresponding correction of approximately +0.50‰ is predicted for ¹⁸O/¹⁶O ratios [Mook and Van der Hock, 1983]. We do not, however, apply these corrections in the analysis of the data below except in summary form in a final table.

ISOTOPIC CALIBRATIONS

Because the isotopic effects reported here are small and mainly detectable only after several years of observations, a stable long-term calibration of the mass spectrometer is essential. We have used a set of primary and laboratory isotopic standards, with a range of 20‰, to calibrate the mass spec-

TABLE 3. Air Samples Collected at Cape Kumukahi

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| Feb. 4, 1980 | 2 | 20 | 340.08 | 338.65 | -7.87 | -1.17 |
| March 3, 1980 | 2 | 21 | 340.78* | 338.72* | -8.54* | -2.16* |
| March 20, 1980 | 2 | 21 | 340.38 | 338.72 | -8.00 | -0.92 |
| March 31, 1980 | 2 | 21 | 340.50 | 338.72 | -8.01 | -0.93 |
| April 14, 1980 | 2 | 21 | 342.34 | 338.80 | -8.00 | -1.03 |
| April 28, 1980 | 2 | 22 | 343.19 | 338.80 | -8.18 | -0.86 |
| May 12, 1980 | 2 | 22 | 342.68 | 338.89 | -8.23 | -1.43 |
| May 27, 1980 | 2 | 22 | 342.86 | 338.89 | -8.07 | -0.83 |
| June 16, 1980 | 3 | 25 | 341.45 | 338.99 | -7.99 | -0.30 |
| June 16, 1980 | 3 | 26 | 341.46 | 338.99 | -8.08 | -0.37 |
| June 30, 1980 | 2 | 26 | 341.04 | 338.99 | -8.04 | -0.31 |
| June 30, 1980 | 2 | 29 | 340.62 | 338.99 | -7.87 | -0.42 |
| June 30, 1980 | 2 | 29 | 340.75 | 338.99 | -7.93 | -0.50 |
| July 3, 1980 | 2 | 29 | 340.27 | 339.10 | -7.92 | -0.62 |
| July 3, 1980 | 2 | 29 | 339.81 | 339.10 | -7.91 | -0.61 |
| July 3, 1980 | 2 | 29 | 340.42 | 339.10 | -7.96 | -0.86 |
| July 3, 1980 | 2 | 31 | 340.06 | 339.10 | -7.92 | -0.59 |
| July 3, 1980 | 2 | 31 | 339.96 | 339.10 | -7.86 | -0.86 |
| July 3, 1980 | 2 | 31 | 339.99 | 339.10 | -7.94 | -0.59 |
| July 3, 1980 | 2 | 31 | 339.34 | 339.10 | -7.88 | -0.72 |
| July 14, 1980 | 2 | 26 | 340.18 | 339.10 | -7.73 | -0.22 |
| July 23, 1980 | 3 | 31 | 337.24 | 339.10 | -7.71 | -0.26 |
| July 23, 1980 | 3 | 31 | 337.32 | 339.10 | -7.71 | -0.52 |
| July 23, 1980 | 3 | 31 | 337.09 | 339.10 | -7.68 | -0.55 |
| July 23, 1980 | 3 | 31 | 337.22 | 339.10 | -7.69 | -0.56 |
| Aug. 18, 1980 | 2 | 26 | 336.30 | 339.23 | -7.61 | -0.41 |
| Sept. 2, 1980 | 2 | 26 | 334.36 | 339.39 | -7.49 | -0.56 |
| Sept. 16, 1980 | 2 | 26 | 335.13 | 339.39 | -7.49 | -0.53 |
| Sept. 29, 1980 | 2 | 26 | 335.80 | 339.39 | -7.57 | -0.65 |
| Oct. 14, 1980 | 2 | 28 | 336.07 | 339.55 | -7.63 | -1.79 |
| Nov. 3, 1980 | 2 | 28 | 339.03 | 339.69 | -7.84 | -1.74 |
| Dec. 2, 1980 | 2 | 28 | 338.45 | 339.81 | -7.71 | -1.06 |
| Jan. 5, 1981 | 2 | 28 | 339.32 | 339.92 | -7.77 | -0.65 |
| Jan. 19, 1981 | 2 | 29 | 342.29 | 339.92 | -7.92 | -0.86 |
| Feb. 2, 1981 | 2 | 29 | 340.87 | 339.99 | -7.83 | -0.43 |
| Feb. 17, 1981 | 2 | 29 | 340.53 | 339.99 | -7.85 | -0.82 |
| March 3, 1981 | 2 | 34 | 342.13 | 340.04 | -7.94 | -0.69 |
| March 16, 1981 | 2 | 34 | 342.91 | 340.04 | -8.05 | -0.86 |
| March 30, 1981 | 2 | 34 | 343.18 | 340.04 | -7.96 | -0.66 |
| April 13, 1981 | 2 | 38 | 342.81 | 340.05 | -7.95 | -0.65 |
| April 27, 1981 | 2 | 38 | 342.52 | 340.05 | -7.88 | -0.57 |
| May 12, 1981 | 2 | 38 | 343.94 | 340.05 | -7.97 | -0.52 |
| May 26, 1981 | 1 | 40 | 343.65 | 340.05 | -8.09 | -0.66 |
| June 16, 1981 | 1 | 40 | 341.96 | 340.08 | -8.12 | -0.98 |
| June 29, 1981 | 2 | 40 | 341.85 | 340.08 | -7.96 | -0.47 |
| July 13, 1981 | 2 | 42 | 338.28 | 340.15 | -7.65 | -0.67 |
| Aug. 4, 1981 | 2 | 42 | 336.93 | 340.26 | -7.51 | -1.11 |
| Aug. 10, 1981 | 2 | 42 | 337.24 | 340.26 | -7.54 | -0.69 |
| Aug. 17, 1981 | 2 | 42 | 338.53 | 340.26 | -7.58 | -0.06 |
| Aug. 24, 1981 | 2 | 42 | 337.22 | 340.26 | -7.50 | -0.33 |
| Aug. 31, 1981 | 2 | 42 | 335.81 | 340.26 | -7.45 | -0.39 |
| Sept. 8, 1981 | 2 | 47 | 335.99 | 340.40 | -7.63 | -0.79 |
| Sept. 15, 1981 | 2 | 47 | 337.11 | 340.40 | -7.76 | -0.77 |
| Sept. 21, 1981 | 2 | 47 | 336.60 | 340.40 | -7.72 | -0.62 |
| Sept. 28, 1981 | 2 | 47 | 336.00 | 340.40 | -7.62 | -0.83 |
| Oct. 6, 1981 | 2 | 47 | 336.18 | 340.54 | -7.59 | -0.90 |
| Oct. 13, 1981 | 2 | 47 | 337.34 | 340.54 | -7.68 | -1.04 |
| Oct. 19, 1981 | 2 | 51 | 338.73 | 340.54 | -7.78 | -1.53 |
| Oct. 26, 1981 | 2 | 51 | 337.90 | 340.54 | -7.63 | -1.07 |
| Nov. 2, 1981 | 2 | 51 | 337.81 | 340.67 | -7.69 | -1.21 |
| Nov. 9, 1981 | 2 | 51 | 338.43 | 340.67 | -7.74 | -1.20 |
| Nov. 16, 1981 | 1 | 51 | 338.58 | 340.67 | -7.69 | -0.89 |
| Dec. 1, 1981 | 1 | 54 | 339.83 | 340.80 | -7.84 | -0.97 |
| Dec. 14, 1981 | 1 | 54 | 338.65 | 340.80 | -7.70 | -0.51 |
| Dec. 29, 1981 | 2 | 56 | 341.67 | 340.80 | -7.99 | -0.98 |
| Jan. 26, 1982 | 2 | 56 | 342.67 | 340.93 | -8.01 | -0.85 |
| Feb. 9, 1982 | 2 | 56 | 341.77 | 341.07 | -7.93 | -0.46 |

*Rejected.

TABLE 4. Air Samples Collected at Fanning Island

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| Aug. 2, 1977 | 2 | 2 | 334.43 | 334.67 | -7.67 | 0.36 |
| Aug. 17, 1977 | 2 | 2 | 334.18 | 334.67 | -7.62 | 0.05 |
| Sept. 5, 1977 | 2 | 2 | 334.04 | 334.74 | -7.59 | 0.29 |
| Sept. 22, 1977 | 2 | 2 | 333.75 | 334.74 | -7.61 | 0.14 |
| Oct. 3, 1977 | 2 | 2 | 333.17 | 334.82 | -7.54 | 0.64 |
| Oct. 19, 1977 | 2 | 2 | 333.01 | 334.82 | -7.62 | 0.45 |
| Nov. 15, 1977 | 2 | 2 | 333.51 | 334.90 | -7.59 | -0.04 |
| Dec. 5, 1977 | 2 | 2 | 333.15 | 335.00 | -7.57 | -0.84 |
| Dec. 15, 1977 | 2 | 2 | 334.00 | 335.00 | -7.60 | 0.05 |
| March 14, 1978 | 2 | 2 | 336.07 | 335.36 | -7.66 | 0.35 |
| April 5, 1978 | 2 | 4 | 337.68 | 335.49 | -7.67 | 0.15 |
| April 13, 1978 | 2 | 4 | 337.35* | 335.49* | -7.98* | -0.39* |
| April 18, 1978 | 2 | 4 | 336.21 | 335.49 | -7.69 | 0.52 |
| May 2, 1978 | 2 | 4 | 337.63 | 335.62 | -7.73 | 0.45 |
| May 17, 1978 | 2 | 4 | 336.23 | 335.62 | -7.65 | 0.39 |
| June 6, 1978 | 2 | 18 | 336.66 | 335.74 | -7.64 | -0.68 |
| June 21, 1978 | 2 | 18 | 336.23 | 335.74 | -7.64 | -0.85 |
| July 7, 1978 | 2 | 16 | 336.75 | 335.87 | -7.77 | -0.44 |
| July 18, 1978 | 2 | 18 | 336.41 | 335.87 | -7.64 | -1.08 |
| Aug. 16, 1978 | 2 | 18 | 335.84 | 335.98 | -7.73 | -1.80 |
| Sept. 4, 1978 | 3 | 10 | 335.42 | 336.08 | -7.66 | 0.09 |
| Sept. 18, 1978 | 2 | 16 | 335.42 | 336.08 | -7.72 | -0.21 |
| Oct. 5, 1978 | 2 | 10 | 334.84 | 336.17 | -7.67 | 0.19 |
| Oct. 17, 1978 | 2 | 18 | 336.54 | 336.17 | -7.79 | -1.34 |
| Nov. 7, 1978 | 2 | 7 | 334.03 | 336.25 | -7.64 | -0.29 |
| Nov. 16, 1978 | 2 | 7 | 335.13 | 336.25 | -7.63 | -0.34 |
| Dec. 6, 1978 | 2 | 7 | 335.14 | 336.33 | -7.66 | -0.29 |
| Feb. 5, 1979 | 2 | 10 | 336.84 | 336.52 | -7.75 | -0.18 |
| Feb. 18, 1979 | 2 | 10 | 337.37 | 336.52 | -7.81 | -0.23 |
| March 6, 1979 | 3 | 13 | 337.45 | 336.63 | -7.71 | -0.45 |
| March 21, 1979 | 3 | 13 | 337.32 | 336.63 | -7.69 | -0.24 |
| April 5, 1979 | 2 | 10 | 338.19 | 336.77 | -7.82 | -0.44 |
| April 23, 1979 | 3 | 10 | 337.81 | 336.77 | -7.82 | -0.42 |
| May 3, 1979 | 3 | 13 | 339.05 | 336.92 | -7.75 | -0.37 |
| May 21, 1979 | 3 | 13 | 339.08 | 336.92 | -7.88 | -0.57 |
| June 6, 1979 | 3 | 16 | 338.10 | 337.09 | -7.84 | -0.56 |
| June 19, 1979 | 3 | 16 | 338.07 | 337.09 | -7.80 | -0.76 |
| July 9, 1979 | 2 | 16 | 336.56 | 337.25 | -7.72 | -0.71 |
| July 18, 1979 | 2 | 18 | 337.55 | 337.25 | -7.77 | -2.75 |
| Aug. 9, 1979 | 2 | 18 | 336.80 | 337.41 | -7.65 | -1.18 |
| Aug. 21, 1979 | 2 | 18 | 336.61 | 337.41 | -7.71 | -0.81 |
| Sept. 4, 1979 | 2 | 18 | 336.88 | 337.59 | -7.69 | -0.26 |
| Sept. 19, 1979 | 2 | 18 | 335.88 | 337.59 | -7.68 | -0.75 |
| Oct. 5, 1979 | 2 | 18 | 336.81 | 337.76 | -7.74 | -0.40 |
| Oct. 16, 1979 | 2 | 18 | 336.52 | 337.76 | -7.70 | -0.69 |
| Nov. 8, 1979 | 2 | 18 | 336.49 | 337.95 | -7.61 | -0.83 |
| Nov. 16, 1979 | 2 | 18 | 336.78 | 337.95 | -7.79 | -0.79 |
| Dec. 4, 1979 | 1 | 38 | 337.84 | 338.13 | -7.76 | -0.95 |
| Dec. 20, 1979 | 2 | 38 | 337.52 | 338.13 | -7.71 | -1.11 |
| Jan. 10, 1980 | 2 | 25 | 338.27 | 338.31 | -7.74 | -0.30 |
| Feb. 7, 1980 | 3 | 25 | 338.84 | 338.49 | -7.84 | -0.31 |
| Feb. 25, 1980 | 3 | 25 | 338.79 | 338.49 | -7.80 | -0.08 |
| March 5, 1980 | 2 | 25 | 338.93 | 338.66 | -7.76 | -0.14 |
| March 25, 1980 | 2 | 25 | 340.34 | 338.66 | -7.90 | -0.28 |
| April 9, 1980 | 2 | 38 | 342.06 | 338.85 | -7.90 | -0.89 |
| April 17, 1980 | 1 | 38 | 343.83 | 338.85 | -7.93 | -0.99 |
| June 5, 1980 | 2 | 25 | 340.42 | 339.18 | -7.88 | -0.24 |
| June 16, 1980 | 2 | 25 | 339.82 | 339.18 | -7.85 | -0.31 |
| Aug. 20, 1980 | 2 | 28 | 339.42 | 339.46 | -7.77 | -0.34 |
| Sept. 4, 1980 | 2 | 28 | 338.20 | 339.58 | -7.71 | -0.17 |
| Sept. 17, 1980 | 2 | 28 | 339.22 | 339.58 | -7.78 | -0.24 |
| Oct. 3, 1980 | 2 | 28 | 338.19 | 339.69 | -7.70 | -0.32 |
| Oct. 18, 1980 | 1 | 28 | 338.56 | 339.69 | -7.72 | -0.77 |
| Nov. 17, 1980 | 2 | 28 | 338.97 | 339.78 | -7.73 | -0.25 |
| Dec. 5, 1980 | 1 | 28 | 338.74 | 339.87 | -7.69 | -0.48 |
| Dec. 16, 1980 | 3 | 29 | 339.07 | 339.87 | -7.62 | -0.43 |
| Jan. 2, 1981 | 2 | 29 | 339.54 | 339.94 | -7.71 | -0.58 |
| Jan. 19, 1981 | 1 | 29 | 340.00 | 339.94 | -7.78 | -0.80 |
| Feb. 3, 1981 | 3 | 29 | 339.86 | 340.02 | -7.67 | -0.32 |
| Feb. 18, 1981 | 3 | 38 | 340.81 | 340.02 | -7.74 | -0.59 |

TABLE 4. (continued)

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| March 4, 1981 | 2 | 38 | 341.66 | 340.08 | -7.87 | -0.86 |
| March 19, 1981 | 1 | 38 | 342.57 | 340.08 | -7.87 | -0.93 |
| April 7, 1981 | 2 | 38 | 341.91 | 340.14 | -7.74 | -0.48 |
| April 18, 1981 | 2 | 38 | 342.70 | 340.14 | -7.88 | -0.65 |
| June 16, 1981 | 2 | 51 | 343.51 | 340.25 | -7.94 | -1.03 |
| July 1, 1981 | 2 | 51 | 341.03 | 340.29 | -7.80 | -0.93 |
| July 15, 1981 | 2 | 51 | 340.62 | 340.29 | -7.78 | -0.72 |
| Aug. 4, 1981 | 2 | 51 | 339.63 | 340.33 | -7.77 | -0.51 |
| Aug. 18, 1981 | 2 | 51 | 339.91 | 340.33 | -7.78 | -0.24 |
| Sept. 2, 1981 | 2 | 51 | 340.33 | 340.37 | -7.79 | -0.29 |
| Sept. 18, 1981 | 2 | 51 | 339.31 | 340.37 | -7.77 | -0.27 |
| Oct. 2, 1981 | 2 | 51 | 338.80 | 340.42 | -7.70 | -0.35 |
| Oct. 16, 1981 | 2 | 56 | 338.88 | 340.42 | -7.72 | -0.46 |
| Nov. 3, 1981 | 2 | 56 | 339.10 | 340.47 | -7.75 | -0.72 |
| Dec. 14, 1981 | 1 | 54 | 340.52 | 340.52 | -7.73 | -0.24 |
| Jan. 4, 1982 | 2 | 54 | 340.97 | 340.57 | -7.79 | -0.12 |
| Jan. 15, 1982 | 2 | 54 | 340.36 | 340.57 | -7.72 | +0.02 |
| Feb. 5, 1982 | 2 | 54 | 341.47 | 340.62 | -7.81 | -0.08 |

*Rejected.

trometer from day to day. Some of these standards have been in use since A.D. 1965. Several additional standards were introduced during this study to increase our control of the isotopic ratios near the values of atmospheric CO₂.

Since our first report on atmospheric CO₂ [Keeling *et al.*, 1979] we have reassessed our data, with the result that the ¹³C/¹²C ratio of our earliest data have been reduced by 0.10‰. The long-term standard record (Figure 1) shows that the accuracy of our calibration is better than ±0.05‰. Repeated runs of the same sample reveals a precision of single analyses of approximately ±0.05‰ for ¹³C/¹²C and ±0.10‰ for ¹⁸O/¹⁶O.

Some problems were encountered with the ¹³C/¹²C data after an almost 6 month shutdown of the mass spectrometer early in A.D. 1980. The CO₂ samples first analyzed after this shutdown showed a consistent 0.15‰ increase in ¹³C/¹²C ratio. This coincided with a +0.05‰ correction after removal of N₂O instead of the +0.18‰ routinely observed. (Separate N₂O analyses of the original air samples gave concentrations in the normal range.) Although we have no conclusive evidence about the true cause of the isotopic shift, the ¹³C/¹²C values of isotopic analysis group numbers 18 and 19 were corrected by -0.15‰. On the basis of analyses of the FGGE air samples, which constitute a large homogeneous set of data obtained during this time period, it appears that the isotopic shift only gradually decreased. Accordingly, analysis group numbers 20–22 have been given a -0.10‰ correction and group number 23 a -0.05‰ correction.

DESCRIPTION OF THE DATA

In Tables 1–5 are summarized the CO₂ concentration and isotopic ratios of all of the air samples collected at the five stations under investigation, a total of 517 samples. Atmospheric CO₂ concentrations are expressed as the mixing ratio in dry air in parts per million by volume (ppm). Following standard practice we express ¹³C/¹²C ratios as the per mil variation from the standard PDB [Mook and Grootes, 1973]. We designate these differential ratios by the symbol δ¹³. The corresponding ¹⁸O/¹⁶O ratios we designate by δ¹⁸ relative to CO₂ prepared from PDB with 100% orthophosphoric acid at

25°C. For four stations where single isotopic samples were obtained on a given day, all isotopic data are reported. In instances in which the air from two or more flasks was combined to obtain a single isotopic CO₂ sample, only the average CO₂ concentration is reported, although it was measured separately for each flask. For La Jolla where up to 12 samples were collected at one time, averages and standard deviation are reported for each day for both concentration data and isotopic ratios. From these replicate data we have established the combined statistical error associated with sampling, CO₂ extraction, and analysis. The standard deviation, averaged for 24 sampling days, is 0.09 ppm for CO₂ concentration, 0.04‰ for δ¹³, and 0.12‰ for δ¹⁸.

Data marked in Tables 1–5 by asterisks have been omitted from further consideration on the basis of large departures in δ¹³ from expectation, determined by inspection. Six of these rejected samples, listed individually in Table 1, were easily identified, because they were in sets of replicate samples collected over a short time at La Jolla, under meteorological conditions such that the CO₂ should have been of constant isotopic composition as was the case for the CO₂ concentration. At the other four stations an additional 15 samples were rejected: 12 for Mauna Loa and one each for the other stations. Several of these rejected samples had abnormal δ¹⁸ values as was the case with four of the La Jolla rejected samples.

At Mauna Loa, regular twice monthly sampling began in February 1980. Prior to then, nine samples were collected in an irregular schedule during mid-1978 and late 1979. These prior data are inconsistent with contemporary data of the other four stations and with the later Mauna Loa data and therefore were removed from further consideration as a group. It is clear that the Mauna Loa isotopic data, from which altogether 12 samples have thus been rejected, are more questionable than data of the other stations. This shortcoming should be kept in mind when comparing the Mauna Loa data with results for the other stations.

Tables 1–5 also list seasonally adjusted CO₂ concentrations at time of sampling (under the heading "CO₂ trend") as discussed below in the section on trend analysis.

TABLE 5. Air Samples Collected at the South Pole

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| March 15, 1977 | 3 | 1 | 330.69 | 331.29 | -7.62 | 0.63 |
| April 1, 1977 | 3 | 1 | 331.05 | 331.43 | -7.67 | 0.92 |
| July 15, 1977 | 3 | 1 | 331.86 | 331.88 | -7.56 | 0.65 |
| Aug. 1, 1977 | 3 | 1 | 332.07 | 332.04 | -7.54 | 0.77 |
| Sept. 15, 1977 | 3 | 1 | 332.77 | 332.20 | -7.67 | 0.85 |
| Oct. 3, 1977 | 3 | 1 | 332.80 | 332.35 | -7.58 | 0.90 |
| Oct. 14, 1977 | 3 | 2 | 332.93 | 332.35 | -7.70 | 0.86 |
| Nov. 1, 1977 | 3 | 2 | 333.17 | 332.51 | -7.78 | 0.89 |
| Nov. 15, 1977 | 3 | 2 | 333.16 | 332.51 | -7.73 | 1.01 |
| Dec. 2, 1977 | 3 | 2 | 333.19 | 332.65 | -7.69 | 0.79 |
| Dec. 18, 1977 | 3 | 2 | 332.92 | 332.65 | -7.87 | 0.27 |
| Jan. 3, 1978 | 3 | 2 | 332.54 | 332.80 | -7.76 | 0.84 |
| Jan. 16, 1978 | 3 | 2 | 332.78 | 332.80 | -7.68 | 1.14 |
| Feb. 1, 1978 | 2 | 2 | 332.38 | 332.95 | -7.68 | 0.90 |
| June 17, 1978 | 3 | 7 | 333.21 | 333.49 | -7.73 | 0.12 |
| July 1, 1978 | 2 | 7 | 333.43 | 333.61 | -7.65 | 0.18 |
| July 16, 1978 | 3 | 7 | 333.58 | 333.61 | -7.64 | 0.16 |
| Aug. 1, 1978 | 3 | 7 | 333.91 | 333.71 | -7.77 | 0.05 |
| Aug. 15, 1978 | 3 | 7 | 334.01 | 333.71 | -7.67 | 0.10 |
| Sept. 1, 1978 | 3 | 7 | 334.46 | 333.79 | -7.71 | 0.27 |
| Sept. 16, 1978 | 3 | 7 | 334.46 | 333.79 | -7.71 | 0.16 |
| Oct. 1, 1978 | 3 | 7 | 334.94 | 333.85 | -7.70 | 0.10 |
| Oct. 15, 1978 | 3 | 7 | 334.56 | 333.85 | -7.74 | 0.30 |
| Nov. 3, 1978 | 3 | 8 | 334.40 | 333.91 | -7.66 | -0.07 |
| Nov. 15, 1978 | 3 | 9 | 334.36 | 333.91 | -7.73 | 0.54 |
| Dec. 1, 1978 | 3 | 8 | 334.22 | 333.97 | -7.66 | 0.02 |
| Dec. 16, 1978 | 2 | 8 | 333.96 | 333.97 | -7.68 | -0.35 |
| Jan. 1, 1979 | 3 | 8 | 333.98 | 334.04 | -7.76 | -0.89 |
| Jan. 15, 1979 | 3 | 8 | 333.69 | 334.04 | -7.69 | 0.19 |
| Feb. 1, 1979 | 3 | 18 | 333.86 | 334.13 | -7.74 | -0.25 |
| Feb. 15, 1979 | 3 | 19 | 333.75 | 334.13 | -7.73 | -0.51 |
| March 1, 1979 | 3 | 19 | 333.43 | 334.23 | -7.75 | -0.71 |
| March 15, 1979 | 3 | 19 | 333.70 | 334.23 | -7.71 | -1.20 |
| April 2, 1979 | 3 | 19 | 333.84 | 334.36 | -7.68 | -0.62 |
| April 16, 1979 | 3 | 19 | 333.94 | 334.36 | -7.69 | -0.41 |
| May 2, 1979 | 2 | 19 | 333.91 | 334.50 | -7.67 | -1.43 |
| May 15, 1979 | 3 | 19 | 334.16 | 334.50 | -7.72 | -0.60 |
| June 15, 1979 | 2 | 20 | 334.20 | 334.66 | -7.81 | -0.64 |
| July 1, 1979 | 3 | 20 | 334.68 | 334.83 | -7.68 | -0.09 |
| July 15, 1979 | 2 | 20 | 334.93 | 334.83 | -7.78 | -1.15 |
| Aug. 1, 1979 | 3 | 20 | 335.22 | 335.00 | -7.68 | 0.02 |
| Aug. 15, 1979 | 2 | 20 | 335.51 | 335.00 | -7.82 | -0.55 |
| Sept. 1, 1979 | 3 | 20 | 335.49 | 335.17 | -7.65 | -0.10 |
| Oct. 1, 1979 | 2 | 20 | 335.79 | 335.34 | -7.85 | -0.72 |
| Oct. 15, 1979 | 2 | 20 | 335.69 | 335.34 | -7.80 | -0.26 |
| Nov. 3, 1979 | 3 | 20 | 336.06 | 334.51 | -7.69 | -0.03 |
| Nov. 15, 1979 | 2 | 20 | 336.20 | 335.51 | -7.87 | -0.52 |
| Dec. 1, 1979 | 3 | 20 | 335.84 | 335.69 | -7.75 | -0.33 |
| Dec. 15, 1979 | 3 | 20 | 335.77 | 335.69 | -7.71 | -0.29 |
| Jan. 1, 1980 | 3 | 20 | 335.91 | 335.88 | -7.72 | -0.15 |
| Jan. 15, 1980 | 2 | 20 | 335.77 | 335.88 | -7.77 | -0.09 |
| Feb. 1, 1980 | 3 | 20 | 335.52 | 336.07 | -7.65 | 0.13 |
| Feb. 15, 1980 | 2 | 20 | 335.57 | 336.07 | -7.77 | -0.49 |
| March 1, 1980 | 2 | 26 | 335.87 | 336.26 | -7.77 | -0.05 |
| March 15, 1980 | 1 | 26 | 335.90 | 336.26 | -7.87 | 0.02 |
| April 1, 1980 | 1 | 26 | 336.02 | 336.46 | -7.85 | 0.03 |
| April 15, 1980 | 3 | 27 | 335.95 | 336.46 | -7.70 | 0.19 |
| May 1, 1980 | 3 | 27 | 336.10 | 336.64 | -7.69 | 0.23 |
| May 15, 1980 | 1 | 27 | 336.81 | 336.64 | -7.74 | 0.25 |
| June 1, 1980 | 1 | 27 | 336.69 | 336.82 | -7.82 | -0.20 |
| June 15, 1980 | 3 | 27 | 336.75 | 336.82 | -7.68 | 0.40 |
| July 1, 1980 | 3 | 27 | 337.13 | 336.98 | -7.81 | 0.13 |
| July 15, 1980 | 3 | 27 | 337.27 | 336.98 | -7.75 | 0.19 |
| Aug. 1, 1980 | 3 | 27 | 337.14 | 337.11 | -7.77 | 0.29 |
| Aug. 15, 1980 | 3 | 27 | 337.61 | 337.11 | -7.73 | 0.32 |
| Sept. 1, 1980 | 2 | 27 | 337.59 | 337.23 | -7.74 | 0.18 |
| Sept. 15, 1980 | 3 | 27 | 337.73 | 337.23 | -7.73 | 0.40 |
| Oct. 1, 1980 | 2 | 27 | 337.60 | 337.33 | -7.75 | 0.14 |
| Oct. 15, 1980 | 3 | 27 | 337.83* | 337.33* | -7.43* | 1.09* |
| Nov. 7, 1980 | 2 | 27 | 337.88 | 337.42 | -7.63 | 0.62 |

TABLE 5. (continued)

| Sampling Date | Number of Combined Samples | Isotopic Analysis Group Number | CO ₂ Concentration, ppm | CO ₂ Trend, ppm | Carbon 13/12, ‰ | Oxygen 18/16, ‰ |
|----------------|----------------------------|--------------------------------|------------------------------------|----------------------------|-----------------|-----------------|
| Nov. 16, 1980 | 2 | 27 | 337.78 | 337.42 | -7.78 | 0.40 |
| Dec. 3, 1980 | 3 | 27 | 337.83 | 337.50 | -7.75 | 0.57 |
| Dec. 15, 1980 | 3 | 31 | 338.03 | 337.50 | -7.77 | -0.02 |
| Jan. 1, 1981 | 3 | 31 | 337.74 | 337.57 | -7.78 | 0.28 |
| Jan. 15, 1981 | 2 | 31 | 337.61 | 337.57 | -7.78 | -0.30 |
| Jan. 15, 1981 | 3 | 31 | 337.65 | 337.57 | -7.77 | 0.07 |
| March 1, 1981 | 3 | 51 | 336.98 | 337.71 | -7.77 | 0.36 |
| March 15, 1981 | 2 | 51 | 337.26 | 337.71 | -7.62 | 0.38 |
| April 1, 1981 | 3 | 51 | 337.10 | 337.78 | -7.75 | 0.33 |
| April 15, 1981 | 3 | 51 | 337.21 | 337.78 | -7.78 | 0.26 |
| May 3, 1981 | 2 | 54 | 337.21 | 337.86 | -7.69 | 0.50 |
| May 15, 1981 | 3 | 54 | 337.37 | 337.86 | -7.76 | 0.22 |
| June 1, 1981 | 2 | 54 | 337.79 | 337.94 | -7.78 | 0.43 |
| June 16, 1981 | 3 | 54 | 337.79 | 337.94 | -7.77 | 0.25 |
| July 1, 1981 | 3 | 54 | 338.02 | 338.00 | -7.78 | 0.34 |
| July 16, 1981 | 3 | 54 | 338.06 | 338.00 | -7.77 | -0.31 |
| Aug. 2, 1981 | 3 | 54 | 338.22 | 338.07 | -7.79 | 0.28 |
| Aug. 16, 1981 | 3 | 54 | 338.41 | 338.07 | -7.70 | 0.48 |
| Sept. 2, 1981 | 3 | 54 | 338.46 | 338.13 | -7.72 | 0.10 |
| Sept. 15, 1981 | 3 | 54 | 338.43 | 338.13 | -7.76 | 0.21 |
| Oct. 1, 1981 | 3 | 54 | 338.85 | 338.18 | -7.80 | 0.42 |
| Oct. 16, 1981 | 2 | 54 | 338.78 | 338.18 | -7.75 | 0.51 |
| Nov. 3, 1981 | 3 | 54 | 338.51 | 338.23 | -7.76 | 0.12 |
| Nov. 29, 1981 | 2 | 54 | 338.58 | 338.23 | -7.71 | 0.46 |
| Dec. 13, 1981 | 3 | 56 | 338.58 | 338.28 | -7.77 | -0.52 |
| Dec. 27, 1981 | 3 | 56 | 338.49 | 338.28 | -7.76 | 0.36 |

*Rejected.

The concentration and δ^{13} data of Tables 1–5 are plotted in Figure 2–6 as a function of time. Linear trends are also shown to aid in comparison with plots of seasonally adjusted data, discussed below. The characteristic seasonal variation in CO₂ concentration is seen to be reflected in the δ^{13} data at the four northern hemisphere stations. At the South Pole, no seasonal variation in δ^{13} is evident, but a long-term trend toward more negative δ^{13} is discernable. A long-term trend in δ^{13} is also vaguely apparent in the locus of points at two other stations having long records (La Jolla and Fanning Island).

Replicate sampling at La Jolla (see Table 1) indicates that oxygen isotopic data in per mil scatter 3 times as much as the carbon data. This larger scatter is partly due to the performance of the mass spectrometer but may also be a result of isotopic exchange with water absorbed on the walls of the 5 l flasks during storage as air samples or isotopic exchange during or after extraction. On one occasion, during conditions of fairly low relative humidity (65%), two samples of air were extracted within 42 and 47 min of sampling to test the possibility of exchange during storage (January 25, 1979, see Table 1). The δ^{13} values are both within 0.02‰ of the average of air samples stored in 5 l glass flasks for 18 days, but the δ^{18} values are 0.23 and 0.25‰ less negative, suggestive of a shift during storage of the air before extraction. It is therefore likely that the δ^{18} analyses, as listed in Tables 1–5, are influenced by both random and systematic errors of the order of 0.20‰ related to sampling and storage procedures.

Furthermore, mass spectrometric analyses during the first months of the project, from July 1978 to May 1979, yield systematically more positive δ^{18} values at all stations than later on, although no procedure of sampling or analysis was knowingly changed near May 1, 1979. Also, isotopic analyses from June to December 1980, after the mass spectrometer had

been repaired, are systematically more negative. We have, therefore, further considered only the mass spectrometric analyses of $^{18}\text{O}/^{16}\text{O}$ obtained after A.D. 1979, excluding analyses with isotopic group numbers 18–23.

The δ^{18} data for 1981 are the most consistent. These data suggest a small seasonal variation at the three northernmost stations with least negative values in the summer, similar to the variation reported by Keeling [1961] but of lower amplitude (Figure 7). Fanning Island and the South Pole show no seasonal trend. The average value of all five stations (approximately 0.0‰ after correction for N₂O) is as expected if the major process controlling $^{18}\text{O}/^{16}\text{O}$ ratios is equilibration with ocean water [Bottinga and Craig, 1969] but the seasonal and latitudinal variations suggest that additional mechanisms also operate.

METHODOLOGY OF TREND ANALYSIS

The overall time dependence of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO₂, as we mentioned in the introduction, is a superposition of two different features. (1). A short-term seasonal variation, already observed by Keeling [1958, 1961], is found in the northern hemisphere and is evidently caused primarily by variations in the metabolic activity of terrestrial plants. This activity produces a maximum CO₂ concentration in April or May and a minimum in August, September, or October. A shift to higher $^{13}\text{C}/^{12}\text{C}$ ratios (less negative δ^{13}) accompanies the decrease in concentration, since land plants preferentially remove $^{12}\text{CO}_2$ from the ambient air, with an isotopic fractionation factor of circa 0.982 [Keeling, 1973, p. 302]. In the southern hemisphere a smaller seasonal variation in CO₂ concentration occurs with the extremes about 6 months out of phase with the northern hemisphere. Until now no southern hemisphere seasonal variation in $^{13}\text{C}/^{12}\text{C}$ has

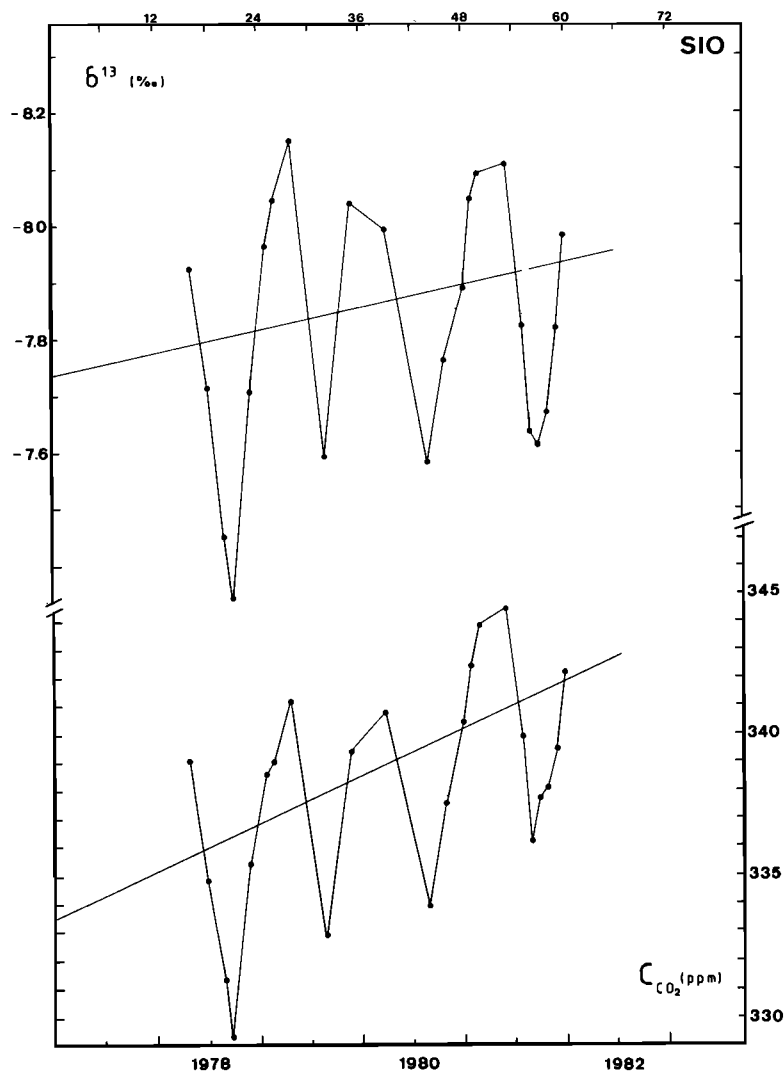


Fig. 2. Time plots of the CO₂ concentration, C_{CO_2} , and isotopic ratio, δ^{13} , obtained from air samples collected at the Scripps Institution of Oceanography, La Jolla (SIO); Mauna Loa Observatory, Hawaii (MLO); Cape Kumukahi, Hawaii (KUM); Fanning Island (FAN); and the South Pole (SPO). Each point is for an individual sampling day. The linear trends in δ^{13} and C_{CO_2} are straight line approximations of long-term trends as discussed in the caption of Figure 10. Short lines connect the SIO data points to show more clearly the seasonal variations in C_{CO_2} and δ^{13} . Numbers on the top border refer to months beginning with January 1977. The δ^{13} values are not corrected for interference from N₂O. (A single point is shown, for both δ^{13} and C_{CO_2} , for January 1979 at SIO as a weighted average, by mistake.)

been reported. (2) A long-term variation or secular trend has occurred in recent years presumably owing to the use of fossil fuels and possibly also to changes in the global biospheric carbon budget. This nonseasonal trend, as estimated by Keeling *et al.* [1979], is so small that it is seen principally as a linear shift with time (see Figures 2–6).

We now consider two features of these time variations. With respect to the seasonal variation, we compare the observed isotopic shift with that predicted on the assumption that it is caused by land plant activity. To characterize the observed shift we compute the isotopic ratio of the CO₂ which appears to have been added to or subtracted from the atmosphere at each station during the course of 1 year. To arrive at the best statistical average for each station, we combine data for all years of each record, first removing the influence of the secular shift. With respect to this secular shift, the records are all too short to expect to see any distinct details of its time rate of change. The increase in CO₂ concentration is clearly not linear in time, however, and the rate at which the isotopic

ratio changes per unit change in CO₂ concentration is likely to vary less with time than the trend in the isotopic ratio. We therefore investigate this quotient over the period of record for each station. At all stations except the South Pole the secular trend can be discerned only if the data are first adjusted to remove the local seasonal cycle. Since, conversely, we need to know the secular trend to determine the seasonal cycle, we are obliged to consider both features simultaneously. To keep the mathematics simple, we have used a procedure of iteration.

The detailed procedure was as follows. First, we made an analysis of the entire CO₂ concentration record for each station by simultaneously fitting four harmonics and a nodal spline to the original observations according to procedures to be reported elsewhere [Bacastow *et al.*, 1983]. From these we tabulated seasonally adjusted CO₂ concentrations at the time of isotopic sampling as listed in Tables 1–5. (We denote these values by the symbol $C_{STR}(t)$, where “STR” indicates “spline trend.”) Then we obtained a linear time trend in CO₂ concentration, $C_{LTR}(t)$, by a least square fit to the smoothed sea-

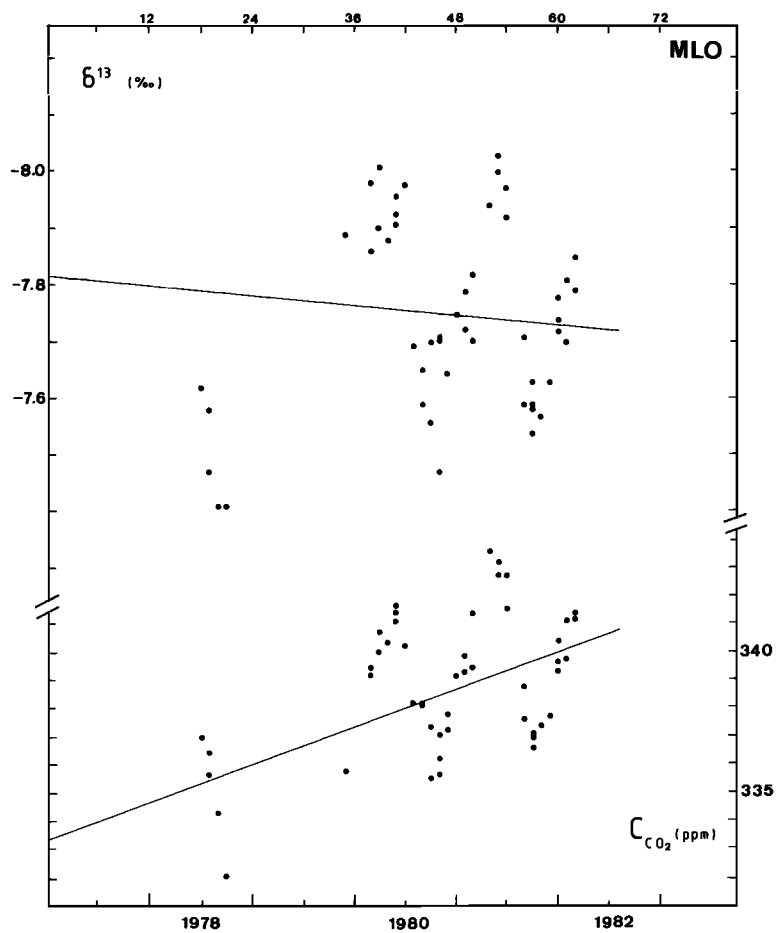


Fig. 3. Same as for Figure 2.

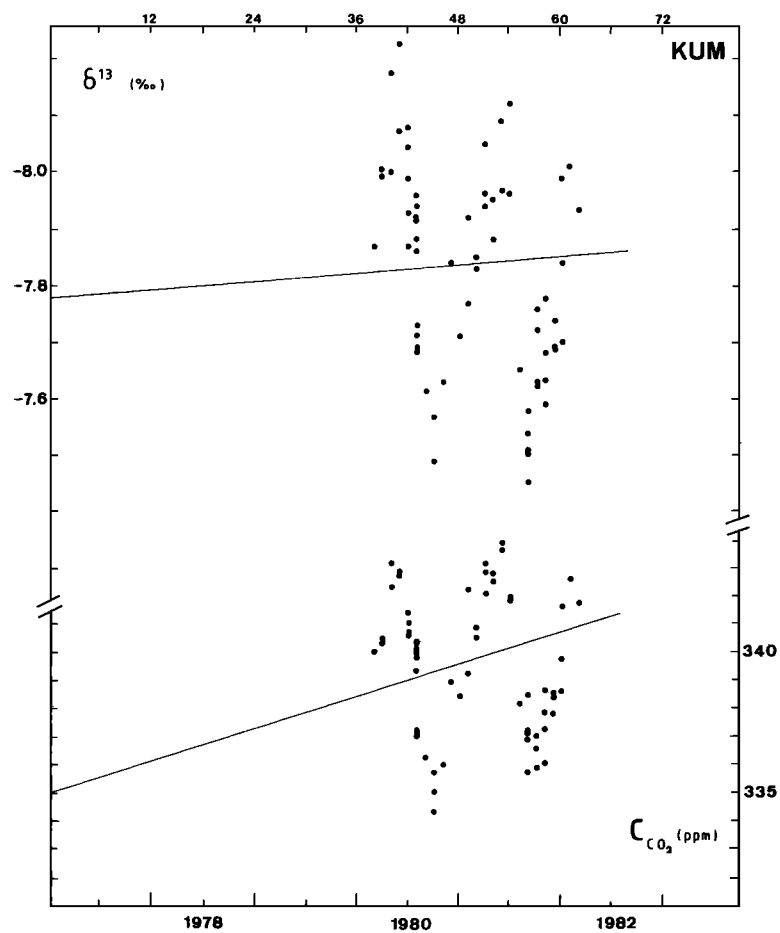


Fig. 4. Same as for Figure 2.

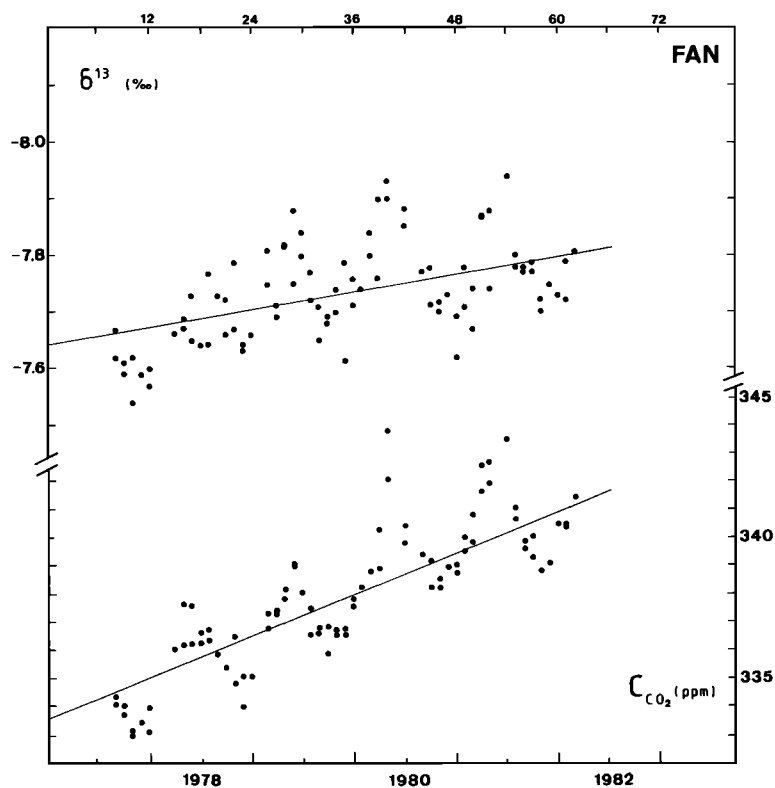


Fig. 5. Same as for Figure 2.

sonally adjusted data, $C_{STR}(t)$. We express the linear time trend by the equation

$$C_{LTR}(t) = a + bt \quad (1)$$

where t denotes time, a and b are constants determined by the fit, and "LTR" indicates "linear trend." We set $t = 0$ for the

beginning of A.D. 1977. Removing this linear trend from the set of observed concentration data, $C(t)$, we obtained a detrended data set

$$C_{DTR}(t) = C(t) - b(t - \bar{t}) \quad (2)$$

$$\bar{t} = (t_0 + t_1)/2$$

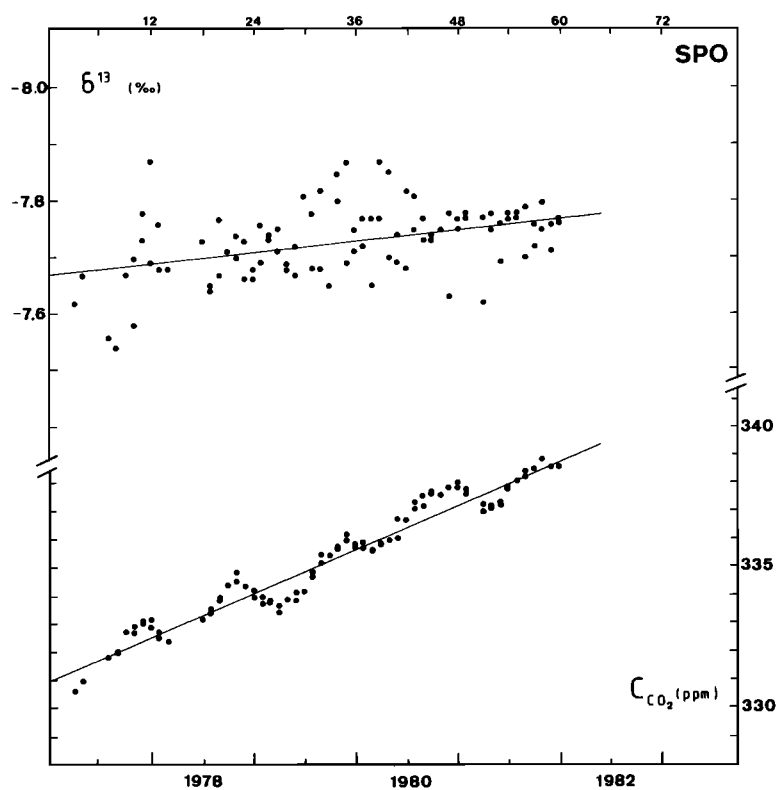


Fig. 6. Same as for Figure 2.

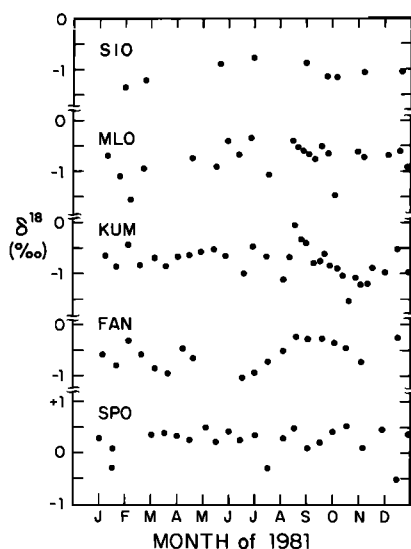


Fig. 7. Time plots of δ^{18} during A.D. 1981 for the same stations as in Figures 2–6. Data are not corrected for interference from N₂O.

where t_0 and t_1 refer to the first and last month of the data set, respectively, and \bar{t} denotes the midpoint date.

We adopted the same procedure to obtain detrended δ^{13} values, except that in this case we fit a straight line to the original data rather than to smoothed seasonally adjusted values. We express the linear time trend by the equation

$$\delta_{\text{LTR}}^{13}(t) = p + qt \quad (3)$$

where p and q are constants determined by the fit. To remove this linear trend from the original δ^{13} data we computed

$$\delta_{\text{DTR}}^{13}(t) = \delta^{13}(t) - q(t - \bar{t}) \quad (4)$$

We next estimated the isotopic composition, δ_I^{13} (I indicates “intercept”), of the CO₂ which appears to be added or subtracted from the air locally to produce the seasonal variation. To find δ_I^{13} we assumed isotopic additivity, that is,

$$C_{\text{DTR}}\delta_{\text{DTR}}^{13} = C_0\delta_0^{13} + \delta_I^{13}(C_{\text{DTR}} - C_0) \quad (5)$$

where subscript 0 specifies an arbitrary reference pair of values, and factors subscripted DTR are time dependent. Solving (5) for δ_{DTR}^{13} we obtained the following linear relation between isotopic ratio and the reciprocal of concentration:

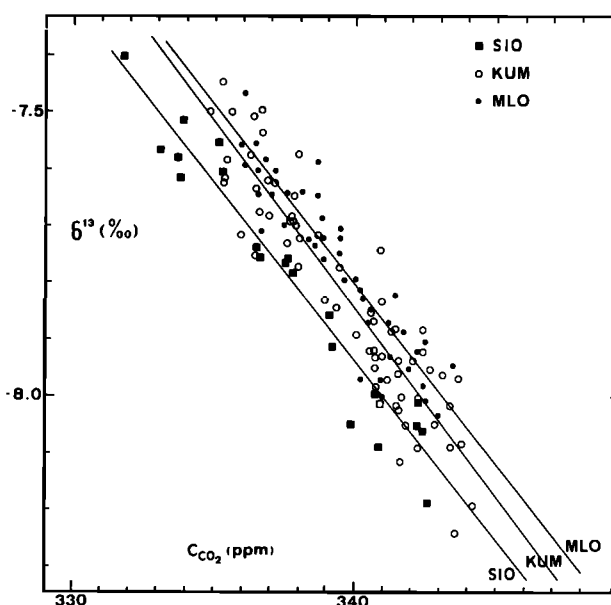


Fig. 8. Relation between δ^{13} and CO₂ concentration with the linear time trends removed (variables designated δ_{DTR}^{13} and C_{DTR} , respectively, in the text) for the same stations as in Figures 2–6. The lines are calculated according to equation (5). The δ^{13} values are not corrected for interference from N₂O.

$$\delta_{\text{DTR}}^{13}(t) = \delta_I^{13} + M/C_{\text{DTR}}(t) \quad (6)$$

where M denotes a constant equal to $C_0(\delta_0^{13} - \delta_I^{13})$ and we indicate by (t) as in (4) that δ_{DTR}^{13} and C_{DTR} are time dependent. We determined δ_I^{13} and M by the method of least squares. Then from the estimates of δ_I^{13} so obtained, we calculated seasonally adjusted δ^{13} values, denoted δ_{SA}^{13} , by correcting the observed δ^{13} data for the corresponding deviation of CO₂ concentration, C , from the spline trend, $C_{\text{STR}}(t)$. We again assumed additivity in the product of concentration and δ^{13} value

$$C\delta^{13} = C_{\text{STR}}\delta_{\text{SA}}^{13} + (C - C_{\text{STR}})\delta_I^{13} \quad (7)$$

where all quantities except δ_I^{13} are functions of the time. Solving for δ_{SA}^{13} , we obtained

$$\delta_{\text{SA}}^{13} = \delta^{13} + \frac{[\delta_I^{13} - \delta^{13}][C_{\text{STR}} - C]}{C_{\text{STR}}} \quad (8)$$

TABLE 6. Coefficients of Equations (1), (3), and (5)

| Station and Sampling Period | Number of Samples | Equation (1) | | Equation (3) | | | Equation (5) | | |
|--|-------------------|--------------|------------------------|------------------|----------------------|-------------------|---------------------|----------------|-------------------|
| | | a, ppm | b, ppm y ⁻¹ | p, ‰ | q, ‰ y ⁻¹ | Standard Error, ‰ | δ_I^{13} , ‰ | M, ppm ‰ | Standard Error, ‰ |
| La Jolla, April 1978 to Dec. 1981 | 204 | 333.56 | 1.684 | -7.738 (0.04) | -0.041 (0.010) | 0.063 | -28.96 (1.13) | 7148 (381) | 0.055 |
| Mauna Loa Observatory Feb. 1980 to Feb. 1982 | 44 | 334.85 | 1.006 | -7.819 (0.06) | +0.018 (0.013) | 0.056 | -29.16 (1.40) | 7260 (474) | 0.058 |
| Cape Kumukahi Feb. 1980 to Feb. 1982 | 66 | 335.06 | 1.150 | -7.782 (0.06) | -0.013 (0.015) | 0.072 | -30.31 (1.17) | 7637 (398) | 0.073 |
| Fanning Island Aug. 1977 to Feb. 1982 | 87 | 333.61 | 1.490 | -7.642 (0.01) | -0.031 (0.004) | 0.050 | -21.34 (1.29) | 4598 (435) | 0.050 |
| South Pole March 1977 to Dec. 1981 | 95 | 331.10 | 1.547 | -7.670 (0.01) | -0.021 (0.005) | 0.058 | -12.72 (4.08) | 1674 (1367) | 0.058 |

Numbers in parentheses are standard errors of the parameter listed immediately above. In equations (1) and (3) $t = 0$ at the beginning of A.D. 1977.

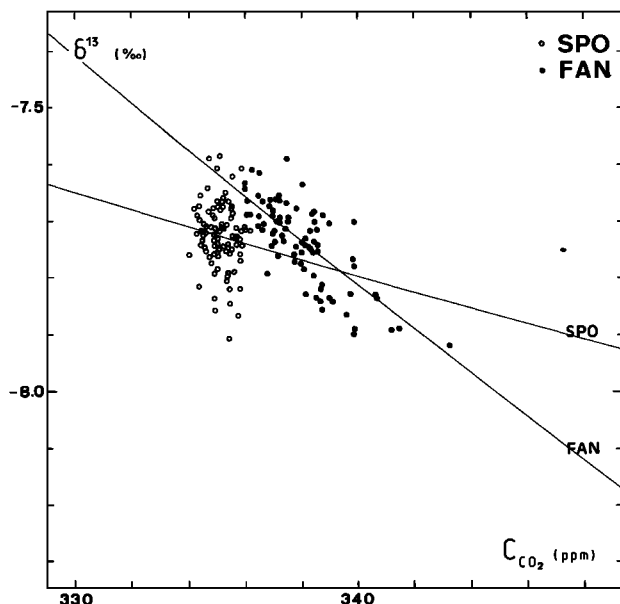


Fig. 9. Same as for Figure 2.

These seasonally adjusted values were now again fit to a linear function of time, resulting in a new linear trend in δ^{13} of the form of (3).

$$\delta_{LTR}^{13}(t) = p' + q't \quad (9)$$

where p' and q' are new constants determined by the new fit. Steps (4), (6), (8), and (9) were now repeated, substituting for q in (4) q' from (9). The calculated parameters converge rapidly, so that three successive iterations were usually sufficient. For the shorter isotopic records at Mauna Loa and Cape Kumukahi we ran six iterations to assure convergence.

RESULTS OF TREND ANALYSIS

The coefficients obtained from the above described analysis are listed in Table 6. Plots of the carbon isotopic ratio versus CO₂ concentration after removing the long-term trend (δ_{DTR}^{13} and C_{DTR} , respectively) are shown in Figures 8 and 9. Monthly averages of the seasonally adjusted data, δ_{SA}^{13} and C_{STR} , are plotted in Figures 10–14. Spline fits of δ_{SA}^{13} are shown to reveal possible nonlinearity in the isotopic trends. The plotted concentrations are averages of C_{STR} for the time of each isotopic sample. As noted above, they were obtained from a spline fit of all available concentration data (often for a longer period than the isotopic record).

The seasonal variation in δ_{DTR}^{13} at any given location correlates closely with the detrended CO₂ concentration, C_{DTR} . Indeed, the standard errors of estimate based on (5) (see Table 6) are so close to the analysis error found from replicate analyses of La Jolla samples (0.04‰, see Table 1) that the only important seasonal parameter to be deduced from the data is the inferred isotopic ratio of the CO₂ added to and withdrawn from the atmosphere during the seasonal cycle.

This quantity, denoted by δ_I^{13} in (5), shows a systematic variation with latitude. For the three northernmost stations, lying between 19° and 31°N, the value of δ_I^{13} is between -28 and -31‰ at the confidence level defined by the standard errors. Fanning Island data imply a less negative value of $-21 \pm 1\%$, while the South Pole data imply a still less negative value of $-12 \pm 4\%$. The seasonal variation in CO₂ concentration at the South Pole is so small that δ_I^{13} is poorly determined. Nevertheless, δ_I^{13} is found to be so much less negative there than elsewhere that the difference is significant.

From analyses of the global CO₂ transport [Pearman and Hyson, 1981; Fung et al., 1983; Keeling and Heimann, 1983] it seems likely that the seasonal variation in CO₂ concentration at the South Pole reflects air-sea exchange as well as terrestrial biospheric activity. Recent estimates of the isotopic frac-

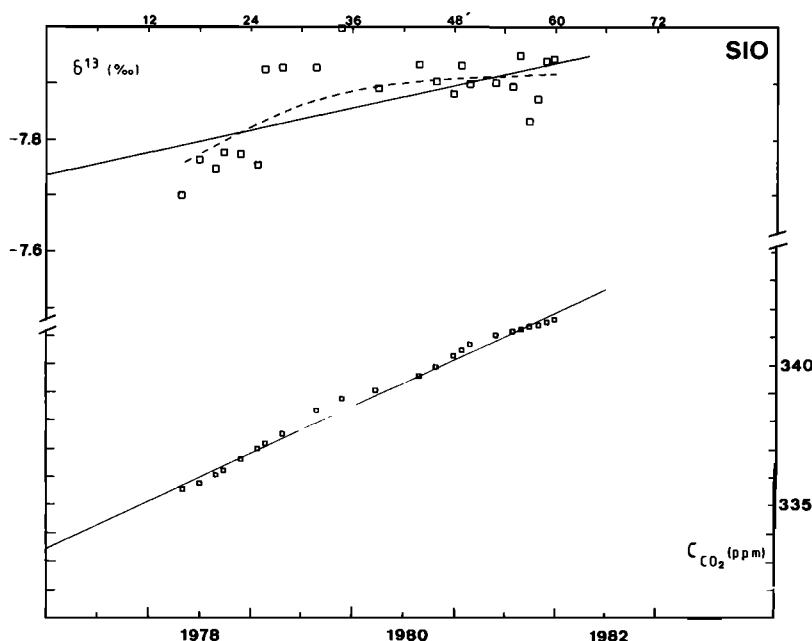


Fig. 10. Time plots of the CO₂ concentration and δ^{13} with the seasonal variations removed (designated C_{STR} and δ_{SA}^{13} , respectively in the text) for the same stations as in Figures 2–6. The dashed lines are spline fits of the monthly averages of δ_{SA}^{13} , shown as large squares. The CO₂ trend is shown by a succession of monthly averages of C_{STR} , denoted by small squares. The straight lines are linear fits to the monthly averages of C_{STR} and δ_{SA}^{13} . These lines are also plotted in Figures 2–6 to aid in a comparison of the two sets of plots.

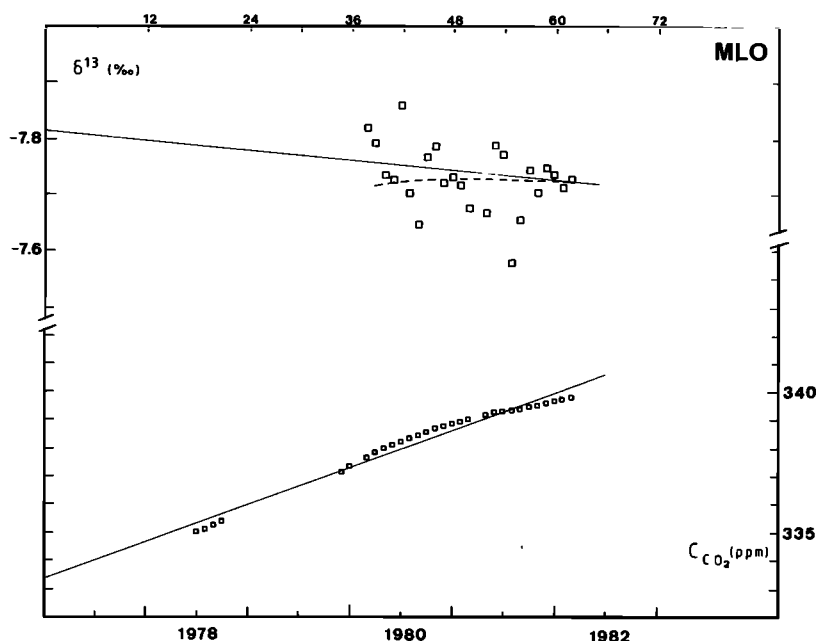


Fig. 11. Same as for Figure 10.

tionation factors for air-sea exchange of CO₂ [Siegenthaler and Münnich, 1981] indicate that very little fractionation is associated with changes in atmospheric CO₂ arising from air-sea exchange. In contrast, land plants fractionate carbon to the extent that their carbon has a δ^{13} value typically in the range -22 to -30‰ [Degens, 1969, p. 313]. The seasonal variation in δ^{13} at the three northernmost stations is thus apt to be almost entirely owing to land plant activity. The implied fractionation, expressed as the per mil difference of δ^{13} from the annual mean of δ^{13} (-7.8‰ in A.D. 1981) is 22‰. For Fanning Island the difference is only 63% as great (13‰) and for the South Pole 23% as great (4‰). On the assumption that air-sea exchange produces negligible fractionation, it would be possible to determine the fraction of the atmospheric CO₂

seasonal variation owing to land plants and air-sea exchange if we knew the phasing of the two oscillations. The phasing, however, is complicated because of the admixture of northern and southern hemisphere components to the seasonal signal and time lags induced by atmospheric mixing. Also, the seasonal variation is characterized by at least two harmonics (6 and 12 months) which have different phase relations. It is thus premature to attempt to resolve the two processes with our isotopic data which do not, by themselves, indicate phasing. The topic will be taken up again, however, in connection with the FGGE data which also show less negative δ^{13} from north to south over the Pacific ocean [Keeling *et al.*, 1983].

The seasonally adjusted CO₂ concentrations for the South Pole, Fanning Island, and La Jolla are seen to rise more

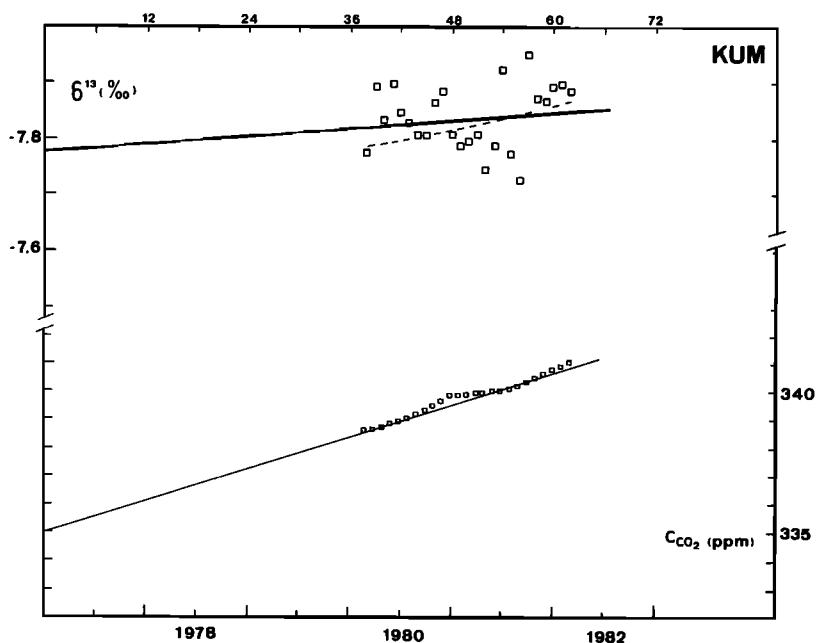


Fig. 12. Same as for Figure 10.

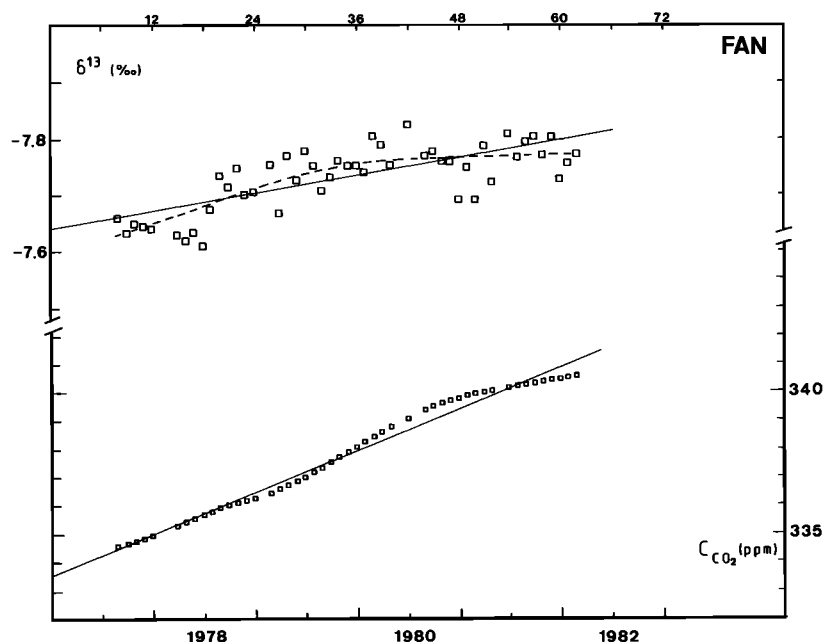


Fig. 13. Same as for Figure 10.

slowly after mid-1980 than in the preceding 2 years. This is a reflection of the tendency for the CO₂ concentration to correlate with a large scale meteorological feature called the Southern Oscillation [Bacastow, 1976, 1979]. A similar slower rise took place at Cape Kumukahi and Mauna Loa Observatory.

Associated with this apparent slowing down in the secular increase in CO₂ concentration since mid-1980 is a lesser shift in δ^{13} with concentration than found for A.D. 1977–1979 and also a lesser shift than found by Keeling *et al.* [1979] between data obtained in A.D. 1955 and 1956 and the earliest of the data reported in our new study (A.D. 1977 and 1978). For La Jolla and Fanning Island from A.D. 1978 to 1982 (see Table 7) the shifts in δ^{13} with concentration are -0.024 ± 0.006 and -0.021 ± 0.003 ‰ ppm⁻¹, respectively. For the South Pole the isotopic shift per ppm is still smaller: -0.014 ± 0.003 ‰

ppm⁻¹. In comparison, the northern hemisphere average estimated by Keeling *et al.* [1979] was 0.031 ± 0.008 ‰ ppm⁻¹ for A.D. 1956–1978. (The isotopic shift originally reported as 0.55‰ has been increased to 0.65‰ to be consistent with our newer calibration of the data for A.D. 1977 and 1978.) The new records reported here are all too short, however, to establish reliably any changes in the long-term global average isotopic shift associated with fossil fuel CO₂.

IDENTIFYING SOURCES AND SINKS OF ATMOSPHERIC CO₂

Since fossil fuel is estimated to have an average δ^{13} value of -27.3 ‰ in A.D. 1980 [Tans, 1981] and is thus distinctly more negative in δ^{13} than CO₂ related to the air-sea exchange (accepting the mechanism of Siegenthaler and Munnich [1981] as correct) ¹³C/¹²C data should be useful separately to identi-

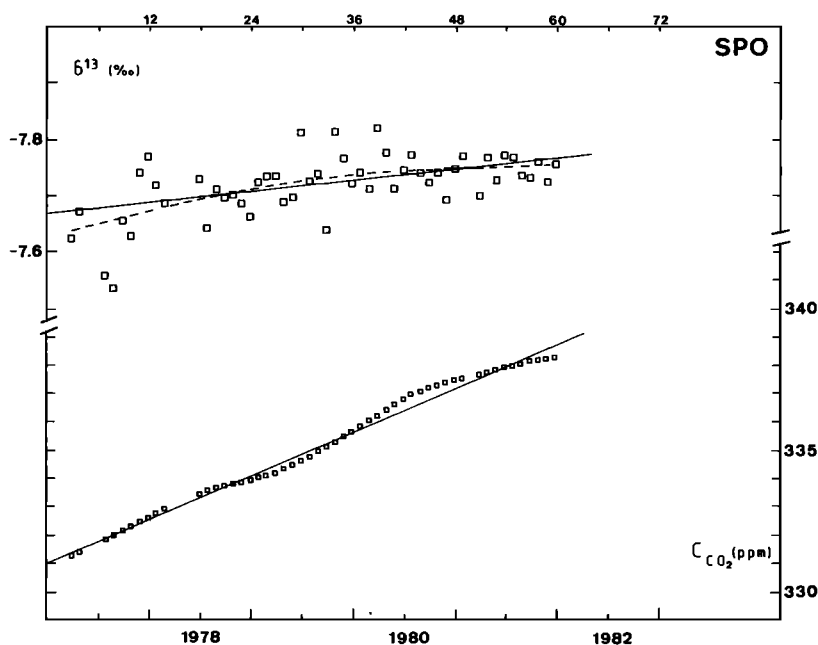


Fig. 14. Same as for Figure 10.

TABLE 7. Change in δ^{13} Relative to Change in Concentration of Atmospheric CO₂

| Station | Record Length, year | $\Delta\delta_{LTR}^{13}$, ‰ y ⁻¹ | ΔC_{LTR} , ppm y ⁻¹ | $\Delta\delta_{LTR}^{13}/\Delta C_{LTR}$, ‰ ppm ⁻¹ |
|-----------------------|---------------------|---|--|--|
| La Jolla | 3.7 | -0.041 ± 0.010 | 1.684 | -0.024 ± 0.006 |
| Mauna Loa Observatory | 2.0 | +0.018 ± 0.013 | 1.006 | +0.018 ± 0.013 |
| Cape Kumukahi | 2.0 | -0.013 ± 0.015 | 1.150 | -0.11 ± 0.013 |
| Fanning Island | 4.5 | -0.031 ± 0.004 | 1.490 | -0.021 ± 0.003 |
| South Pole | 4.7 | -0.021 ± 0.005 | 1.547 | -0.014 ± 0.003 |

fy oceanic exchange and fossil fuel combustion as causes of the north-south gradient in atmospheric CO₂. Wherever a variation in CO₂ concentration is not accompanied by a shift in δ^{13} as large as predicted by transfer of fossil fuel or plant carbon (which on average is practically indistinguishable in δ^{13} from fossil fuel), oceanic exchange is likely to be influencing the CO₂ distribution. A comparison of the mean-annual north-south profiles of atmospheric CO₂ concentration and δ^{13} (Figure 15) shows that δ^{13} varies but slightly from the South Pole to the latitude of Hawaii. On the other hand, the δ^{13} for La Jolla (33°N) is distinctly more negative than for the South Pole as expected from the predominance of fossil fuel combustion in the northern hemisphere. Thus it appears likely that both oceanic CO₂ exchange and fossil fuel CO₂ help produce the north-south profile in CO₂ concentration, with oceanic exchange predominating in the equatorial region.

Let us consider the data more closely. In Table 8 we list the seasonally adjusted CO₂ concentration and δ^{13} values, already shown plotted as north-south profiles in Figure 15. To obtain the CO₂ concentration for January 1, 1980, we accepted values of C_{STR} given directly by spline fits for each station as the best available estimates. (The straight line approximations to C_{STR} , given by (1), closely approximate, but do not coincide, with these values.) We then computed δ_{SA}^{13} by (3) to obtain corresponding isotopic values for the same date. Again, rather than to accept the straight line estimate we made a slight refinement: we assumed that the relation between δ_{SA}^{13} and C_{STR} given by combining (1) and (3) was more likely to be valid than the direct estimates based solely on (3) (i.e., we

eliminated t between (1) and (3) and solved the resulting expression for δ_{SA}^{13} in terms of the January 1, 1980, values of C_{STR}). The refinement shifted the isotopic values by, at most, 0.006‰.

The seasonally adjusted CO₂ concentration at La Jolla on January 1, 1980 (338.97 ppm) was 3.19 ppm higher than for the South Pole (335.78 ppm) whereas the seasonally adjusted isotopic ratio, δ_{SA}^{13} was 0.136‰ more negative. These two shifts indicate that δ^{13} for the net amount of carbon transferred to the atmosphere to produce the higher concentration in the north was about -22‰. This result implies that the CO₂ to produce this higher concentration was coming largely from land plants or from fossil fuel rather than from the oceans. In contrast, between the South Pole and Fanning Island (4°N) the concentration increased northward by 2.44 ppm while δ^{13} decreased by only 0.004‰. This implies a δ^{13} of the transferred carbon of -8‰ characteristic of an oceanic source producing the northward increase in CO₂. The corresponding δ^{13} between the South Pole and Mauna Loa is -15‰ suggesting a mixture of oceanic and fossil fuel (or plant) carbon as the cause of the gradient. The three station pairs together suggest an oceanic source in the tropics and a fossil fuel (or plant) source further north.

This result is of special interest in clarifying the importance of the land biosphere to the recent perturbation of the carbon cycle; it implies that the terrestrial biosphere contributes little or no CO₂ to the flux which produced the peak in atmospheric CO₂ near the equator in the central Pacific ocean. If the isotopic data of Table 8 reflect zonal averages, they further imply an absence of any large net source of atmospheric CO₂ from deforestation in the tropics in A.D. 1980. Isotopic data, on the other hand, do not allow an estimate of what part of the source in the northern hemisphere is from plants since fossil fuel carbon confuses the picture.

Cape Kumukahi furnishes additional isotopic data near 20°N, but the data appear to be biased. The CO₂ concentration there is consistently higher than at the nearby

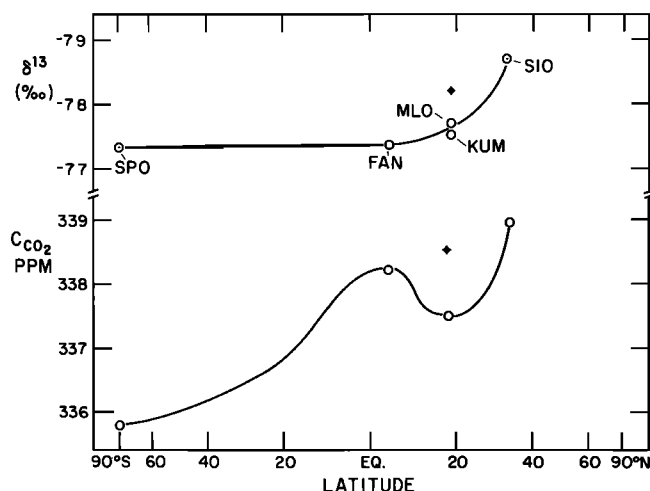


Fig. 15. North-south seasonally adjusted distributions of CO₂ concentration and δ^{13} for January 1, 1980. The smooth curves are drawn freely between the points. The diamond symbols denote values for Cape Kumukahi before adjustment to the CO₂ concentration of Mauna Loa Observatory.

TABLE 8. Seasonally Adjusted CO₂ Concentration and δ^{13} for January 1, 1980

| Station | C_{STR}^* | $\delta_{SA}^{13}\dagger$ | Adjusted | |
|-----------------------|-------------|---------------------------|-----------|--------------------|
| | | | C_{STR} | δ_{SA}^{13} |
| La Jolla | 338.97 | -7.870 | | |
| Mauna Loa Observatory | 337.51 | -7.771 | | |
| Cape Kumukahi | 338.53 | -7.821 | 337.51‡ | -7.753 |
| Fanning Island | 338.22 | -7.738 | | |
| South Pole | 335.78 | -7.734 | | |

*CO₂ concentration from spline trend.

† δ^{13} from equation (3).

‡Assumed to be the same as at Mauna Loa Observatory. See text.

TABLE 9. Summary of Isotopic Data for January 1, 1980

| Station | Latitude | Seasonally Adjusted CO ₂ Concentration, ppm | Seasonally Adjusted δ^{13} , ‰ | δ^{13} of Seasonal Component, ‰ | Annual Mean δ^{18} , ‰ |
|-----------------------|----------|--|--|---|--|
| La Jolla | 32.9°N | 339.0 | -7.64 | -28.7 | -0.60 |
| Mauna Loa Observatory | 19.5°N | 337.5 | -7.55 | -28.9 | -0.09 |
| Cape Kumukahi | 19.5°N | 338.5 | -7.60 | -30.1 | -0.23 |
| Fanning Island | 4.0°N | 338.2 | -7.51 | -21.1 | +0.02 |
| South Pole | 90.0°S | 335.8 | -7.51 | -12.5 | +0.71 |

Data for CO₂ concentration and δ^{13} are from Tables 6 and 8; δ^{13} values are raised 0.225‰ and δ^{18} by 0.50‰ to correct for presence of N₂O.

Mauna Loa Observatory. The difference in δ_{SA}^{13} is -0.050‰. The corresponding difference predicted for a fossil fuel or land plant carbon source is -0.059‰, and for an oceanic source it is close to zero. The isotopic data thus suggest that CO₂ from plants or fossil fuel causes the concentration difference. Assuming this, we have computed the period average of δ_{SA}^{13} which would have been observed at Cape Kumukahi if the CO₂ concentration there had been the same as at Mauna Loa Observatory. Specifically, we assumed that the concentration is elevated because of added CO₂ having δ^{13} equal to δ_1^{13} for Cape Kumukahi as listed in Table 6 (-30.31‰). The corrected value of δ_{SA}^{13} is listed in Table 8 and plotted in Figure 15. Consistent with our hypothesis, this corrected value is close (within 0.02‰) to the δ_{SA}^{13} value for Mauna Loa Observatory.

Shipboard samples collected on the FGGE expedition also suggest that the samples collected at Cape Kumukahi are contaminated, but to a lesser extent since the shipboard data, referred to January 1, 1980, are 0.20 ppm higher than the corresponding concentrations for Mauna Loa Observatory. Also, the FGGE data suggest that the concentration data for Fanning Island are on average too high by 0.54 ppm. Since these FGGE expedition data offer considerable additional information to establish the north-south trend in atmospheric CO₂, we defer further discussion of this topic until the FGGE data can be closely examined in another article. We also defer a reassessment of the secular change in δ^{13} since A.D. 1956 which was computed by Keeling *et al.* [1979] without regard for any latitudinal gradient.

CONCLUDING REMARKS

From 4 years of records of the ¹³C/¹²C ratio of atmospheric CO₂ at La Jolla, Fanning Island, and the South Pole, it is evident that our sampling and analysis methods are adequate to document changes in isotopic ratio associated with long-term trends in the global carbon cycle, for example with the combustion of fossil fuels. From the analyses of samples collected twice per month at these three stations, and at two additional stations with shorter records, we have detected variations in isotopic ratio to a precision approaching 0.01‰. We find small variations in seasonally adjusted isotopic ratios both with respect to year to year variations and a north-south trend.

We are not yet certain of the magnitude of the correction to be applied for interference from N₂O in the samples of CO₂ extracted from air, and therefore we have carried out our analysis of the data without applying a correction. To facilitate the use of these data for other studies, however, especially where fractionation with respect to other chemical phases may

be under consideration, we have prepared a summary in Table 9 with an N₂O correction applied. The δ^{13} data are abstracted from Tables 6 and 8. The δ^{18} values were determined by first averaging the individual analyses of A.D. 1980-1982 (Tables 1-5) for each month of each year (usually a pair of values), then from these calculating unweighted monthly means based on all 3 years, and finally averaging these to obtain an annual mean for each station, ignoring months without data. We estimate that the precision in the δ^{13} data presented in Table 9 is of the order of 0.02‰, the accuracy of the order of 0.10‰, not taking into account any systematic errors associated with the N₂O correction. The precision and accuracy of the CO₂ concentration data are approximately 0.1 and 0.2 ppm, respectively. The reliability of the δ^{18} data is not well established but probably of the order of 0.5‰.

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REFERENCES

- Bacastow, R. B., Modulation of atmospheric carbon dioxide by the Southern Oscillation, *Nature*, 261, 116-118, 1976.
- Bacastow, R. B., Dip in the atmospheric CO₂ level during the mid-1960's, *J. Geophys. Res.*, 84, 3108-3114, 1979.
- Bacastow, R. B., C. D. Keeling, and T. P. Whorf, Seasonal amplitude increase in atmospheric CO₂ concentration at Mauna Loa Observatory, Hawaii, 1959-1982, *J. Geophys. Res.*, in press, 1983.
- Bottinga, Y., and H. Craig, Oxygen isotope fractionation between CO₂ and water, and the isotopic composition of marine atmospheric CO₂, *Earth Planet. Sci. Lett.*, 5, 285-295, 1969.
- Craig, H., and C. D. Keeling, The effects of atmospheric N₂O on the measured isotopic composition of atmospheric CO₂, *Geochim. Cosmochim. Acta*, 27, 549-551, 1963.
- Degens, E. T., Biogeochemistry of stable carbon isotopes, in *Organic Chemistry Methods and Results*, edited by G. Eglinton and M. T. J. Murphy, pp. 304-329, Springer-Verlag, New York, 1969.
- Fung, I., K. Prentice, E. Matthews, J. Lerner, and G. Russell, A 3-D tracer model study of atmospheric CO₂: Response to seasonal exchange with the terrestrial biosphere, *J. Geophys. Res.*, 88, 1281-1294, 1983.
- Keeling, C. D., The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas, *Geochim. Cosmochim. Acta*, 13, 322-334, 1958.
- Keeling, C. D., The concentration and isotopic abundances of carbon dioxide in rural and marine air, *Geochim. Cosmochim. Acta*, 24, 277-298, 1961.
- Keeling, C. D., The carbon dioxide cycle: Reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and

- land plants, chapter 6, in *Chemistry of the Lower Atmosphere*, edited by S. I. Rasool, pp. 251–329, Plenum, New York, 1973.
- Keeling, C. D., and M. Heimann, Meridional eddy diffusion model of the transport of atmospheric carbon dioxide, 2, The mean annual carbon cycle, *J. Geophys. Res.*, in press, 1983.
- Keeling, C. D., T. B. Harris, and E. M. Wilkins, Concentration of atmospheric carbon dioxide at 500 and 700 millibars, *J. Geophys. Res.*, 73, 4511–4528, 1968.
- Keeling, C. D., W. G. Mook, and P. P. Tans, Recent trends in the ¹³C/¹²C ratio of atmospheric carbon dioxide, *Nature*, 277, 121–123, 1979.
- Keeling, C. D., R. B. Bacastow, and P. P. Tans, Predicted shift in the ¹³C/¹²C ratio of atmospheric carbon dioxide, *Geophys. Res. Lett.*, 7, 505–508, 1980.
- Keeling, C. D., A. F. Carter, and W. G. Mook, Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of atmospheric carbon dioxide, 2, Results from oceanographic cruises in the tropical Pacific Ocean, *J. Geophys. Res.*, in press, 1983.
- Mook, W. G., and P. M. Grootes, The measuring procedures and corrections for the high-precision mass-spectrometric analysis of isotopic abundance ratios, especially referring to carbon, oxygen and nitrogen, *Int. J. Mass Spectrom. Ion Phys.*, 12, 273–298, 1973.
- Mook, W. G., and S. van der Hoek, The N₂O correction in the carbon and oxygen isotopic analysis of atmospheric CO₂, *Isotope Geosc.*, 1, 1983.
- Pearman, G. I., and P. Hyson, The annual variation of atmospheric CO₂ concentration observed in the northern hemisphere, *J. Geophys. Res.*, 86, 9839–9843, 1981.
- Siegenthaler, U., and K. O. Münnich, ¹³C/¹²C fractionation during CO₂ transfer from air to sea, in *Carbon Cycle Modelling*, edited by B. Bolin, pp. 249–257, John Wiley, New York, 1981.
- Tans, P., ¹³C/¹²C of industrial CO₂, in *Carbon Cycle Modelling*, edited by B. Bolin, pp. 127–129, John Wiley, New York, 1981.
- Weiss, R. F., The temporal and spatial distribution of tropospheric nitrous oxide, *J. Geophys. Res.*, 86, 7185–7195, 1981.
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